Libby Asbestos Project
Libby, Montana

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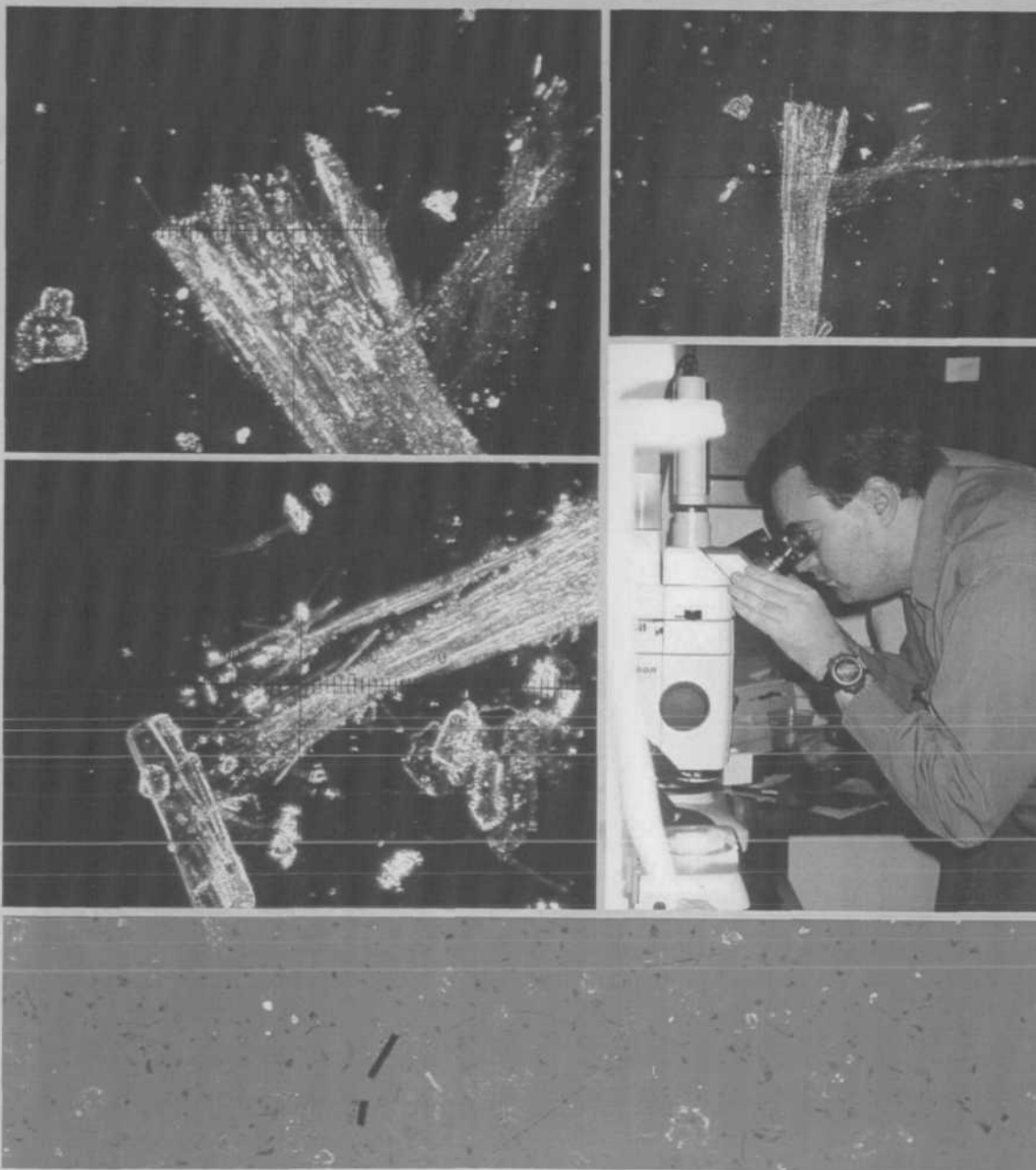55 Broadway, DTS-33
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Designation: D 5755 – 03

Standard Test Method for
Microvacuum Sampling and Indirect Analysis of Dust by Transmission Electron Microscopy for Asbestos Structure Number Surface Loading[1]

This standard is issued under the fixed designation D 5755; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers a procedure to (*a*) identify asbestos in dust and (*b*) provide an estimate of the surface loading of asbestos in the sampled dust reported as the number of asbestos structures per unit area of sampled surface.

1.1.1 If an estimate of the asbestos mass is to be determined, the user is referred to Test Method D 5756.

1.2 This test method describes the equipment and procedures necessary for sampling, by a microvacuum technique, non-airborne dust for levels of asbestos structures. The non-airborne sample is collected inside a standard filter membrane cassette from the sampling of a surface area for dust which may contain asbestos.

1.2.1 This procedure uses a microvacuuming sampling technique. The collection efficiency of this technique is unknown and will vary among substrates. Properties influencing collection efficiency include surface texture, adhesiveness, electrostatic properties and other factors.

1.3 Asbestos identified by transmission electron microscopy (TEM) is based on morphology, selected area electron diffraction (SAED), and energy dispersive X-ray analysis (EDXA). Some information about structure size is also determined.

1.4 This test method is generally applicable for an estimate of the surface loading of asbestos structures starting from approximately 1000 asbestos structures per square centimetre.

1.4.1 The procedure outlined in this test method employs an indirect sample preparation technique. It is intended to disperse aggregated asbestos into fundamental fibrils, fiber bundles, clusters, or matrices that can be more accurately quantified by transmission electron microscopy. However, as with all indirect sample preparation techniques, the asbestos observed for quantification may not represent the physical form of the asbestos as sampled. More specifically, the procedure described neither creates nor destroys asbestos, but it may alter the physical form of the mineral fibers.

1.5 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*
D 1193 Specification for Reagent Water[2]
D 3195 Practice for Rotameter Calibration[3]
D 3670 Guide for Determination of Precision and Bias of Methods of Committee D22[3]
D 5756 Test Method for Microvacuum Sampling and Indirect Analysis of Dust by Transmission Electron Microscopy for Asbestos Mass Surface Loading[3]
D 6620 Practice for Determining a Detection Limit for Asbestos Measurements Based on Counts[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *asbestiform*—a special type of fibrous habit in which the fibers are separable into thinner fibers and ultimately into fibrils. This habit accounts for greater flexibility and higher tensile strength than other habits of the same mineral. For more information on asbestiform mineralogy, see Refs (1),[4] (2) and (3).

3.1.2 *asbestos*—a collective term that describes a group of naturally occurring, inorganic, highly fibrous, silicate dominated minerals, which are easily separated into long, thin, flexible fibers when crushed or processed.

[2] *Annual Book of ASTM Standards*, Vol 11.01.
[3] *Annual Book of ASTM Standards*, Vol 11.03.
[4] The boldface numbers in parentheses refer to the list of references at the end of this test method.

3.1.2.1 *Discussion*—Included in the definition are the asbestiform varieties of: serpentine (chrysotile); riebeckite (crocidolite); grunerite (grunerite asbestos); anthophyllite (anthophyllite asbestos); tremolite (tremolite asbestos); and actinolite (actinolite asbestos). The amphibole mineral compositions are defined according to nomenclature of the International Mineralogical Association (3).

Asbestos	Chemical Abstract Service No.[5]
Chrysotile	12001-29-5
Crocidolite	12001-28-4
Grunerite Asbestos	12172-73-5
Anthophyllite Asbestos	77536-67-5
Tremolite Asbestos	77536-68-6
Actinolite Asbestos	77536-66-4

3.1.3 *fibril*—a single fiber that cannot be separated into smaller components without losing its fibrous properties or appearance.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *aspect ratio*—the ratio of the length of a fibrous particle to its average width.

3.2.2 *bundle*—a structure composed of three or more fibers in a parallel arrangement with the fibers closer than one fiber diameter to each other.

3.2.3 *cluster*—a structure with fibers in a random arrangement such that all fibers are intermixed and no single fiber is isolated from the group; groupings of fibers must have more than two points touching.

3.2.4 *debris*—materials that are of an amount and size (particles greater than 1 mm in diameter) that can be visually identified as to their source.

3.2.5 *dust*—any material composed of particles in a size range of <1 mm.

3.2.6 *fiber*—a structure having a minimum length of 0.5 μm, an aspect ratio of 5:1 or greater, and substantially parallel sides (4).

3.2.7 *fibrous*—of a mineral composed of parallel, radiating, or interlaced aggregates of fibers, from which the fibers are sometimes separable. That is, the crystalline aggregate may be referred to as fibrous even if it is not composed of separable fibers, but has that distinct appearance. The term fibrous is used in a general mineralogical way to describe aggregates of grains that crystallize in a needle-like habit and appear to be composed of fibers. Fibrous has a much more general meaning than asbestos. While it is correct that all asbestos minerals are fibrous, not all minerals having fibrous habits are asbestos.

3.2.8 *indirect preparation*—a method in which a sample passes through one or more intermediate steps prior to final filtration.

3.2.9 *matrix*—a structure in which one or more fibers, or fiber bundles that are touching, are attached to, or partially concealed by a single particle or connected group of non-fibrous particles. The exposed fiber must meet the fiber definition (see 3.2.6).

3.2.10 *structures*—a term that is used to categorize all the types of asbestos particles which are recorded during the analysis (such as fibers, bundles, clusters, and matrices). Final

results of the test are always expressed in asbestos structures per square centimetre.

4. Summary of Test Method

4.1 The sample is collected by vacuuming a known surface area with a standard 25 or 37 mm air sampling cassette using a plastic tube that is attached to the inlet orifice which acts as a nozzle. The sample is transferred from inside the cassette to an aqueous suspension of known volume. Aliquots of the suspension are then filtered through a membrane. A section of the membrane is prepared and transferred to a TEM grid using the direct transfer method. The asbestiform structures are identified, sized, and counted by TEM, using SAED and EDXA at a magnification of 15 000 to 20 000X.

5. Significance and Use

5.1 This microvacuum sampling and indirect analysis method is used for the general testing of non-airborne dust samples for asbestos. It is used to assist in the evaluation of dust that may be found on surfaces in buildings such as ceiling tiles, shelving, electrical components, duct work, carpet, etc. This test method provides an index of the surface loading of asbestos structures in the dust per unit area analyzed as derived from a quantitative TEM analysis.

5.1.1 This test method does not describe procedures or techniques required to evaluate the safety or habitability of buildings with asbestos-containing materials, or compliance with federal, state, or local regulations or statutes. It is the user's responsibility to make these determinations.

5.1.2 At present, no relationship has been established between asbestos-containing dust as measured by this test method and potential human exposure to airborne asbestos. Accordingly, the users should consider other available information in their interpretation of the data obtained from this test method.

5.2 This definition of dust accepts all particles small enough to pass through a 1 mm (No. 18) screen. Thus, a single, large asbestos containing particle(s) (from the large end of the particle size distribution) dispersed during sample preparation may result in anomalously large asbestos surface loading results in the TEM analyses of that sample. It is, therefore, recommended that multiple independent samples are secured from the same area, and that a minimum of three samples be analyzed by the entire procedure.

6. Interferences

6.1 The following minerals have properties (that is, chemical or crystalline structure) which are very similar to asbestos minerals and may interfere with the analysis by causing a false positive to be recorded during the test. Therefore, literature references for these materials must be maintained in the laboratory for comparison to asbestos minerals so that they are not misidentified as asbestos minerals.

6.1.1 *Antigorite.*

6.1.2 *Palygorskite (Attapulgite).*

6.1.3 *Halloysite.*

6.1.4 *Pyroxenes.*

6.1.5 *Sepiolite.*

6.1.6 *Vermiculite scrolls.*

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[5] The non-asbestiform variations of the minerals indicated in 5.1.3 have different Chemical Abstract Service (CAS) numbers.

6.1.7 *Fibrous talc.*

6.1.8 *Hornblende* and other amphiboles other than those listed in 3.1.2.

6.2 Collecting any dust particles greater than 1 mm in size in this test method may cause an interference and, therefore, must be avoided.

7. Materials and Equipment

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.[6]

7.2 *Transmission Electron Microscope (TEM)*, an 80 to 120 kV TEM, capable of performing electron diffraction, with a fluorescent screen inscribed with calibrated gradations, is required. The TEM must be equipped with energy dispersive X-ray spectroscopy (EDXA) and it must have a scanning transmission electron microscopy (STEM) attachment or be capable of producing a spot size of less than 250 nm in diameter in crossover.

7.3 *Energy Dispersive X-ray System (EDXA)*.

7.4 *High Vacuum Carbon Evaporator*, with rotating stage.

7.5 *High Efficiency Particulate Air (HEPA)*, filtered negative flow hood.

7.6 *Exhaust or Fume Hood.*

7.7 *Particle-free Water* (ASTM Type II, see Specification D 1193).

7.8 *Glass Beakers* (50 mL).

7.9 *Glass Sample Containers*, with wide mouth screw cap (200 mL) or equivalent sealable container (height of the glass sample container should be approximately 13 cm high by 6 cm wide).

7.10 *Waterproof Markers.*

7.11 *Forceps* (tweezers).

7.12 *Ultrasonic Bath*, table top model (100 W).

7.13 *Graduated Pipettes* (1, 5, 10 mL sizes), glass or plastic.

7.14 *Filter Funnel*, either 25 mm or 47 mm, glass or disposable. Filter funnel assemblies, either glass or disposable plastic, and using either a 25 mm or 47 mm diameter filter.

7.15 *Side Arm Filter Flask*, 1000 mL.

7.16 *Mixed Cellulose Ester (MCE) Membrane Filters*, 25 or 47 mm diameter, ≤0.22 µm and 5 µm pore size.

7.17 *Polycarbonate (PC) Filters*, 25 or 47 mm diameter, ≤0.2 µm pore size.

7.18 *Storage Containers*, for the 25 or 47 mm filters (for archiving).

7.19 *Glass Slides*, approximately 76 by 25 mm in size.

7.20 *Scalpel Blades*, No. 10, or equivalent.

7.21 *Cabinet-type Desiccator*, or low temperature drying oven.

7.22 *Chloroform*, reagent grade.

7.23 *Acetone*, reagent grade.

7.24 *Dimethylformamide (DMF).*

7.25 *Glacial Acetic Acid.*

7.26 *1-methyl-2-pyrrolidone.*

7.27 *Plasma Asher*, low temperature.

7.28 *pH Paper.*

7.29 *Air Sampling Pump*, low volume personal-type, capable of achieving a flow rate of 1 to 5 L/min.

7.30 *Rotameter.*

7.31 *Air Sampling Cassettes*, 25 mm or 37 mm, containing 0.8µ m or smaller pore size MCE or PC filters.

7.32 *Cork Borer*, 7 mm.

7.33 *Non-Asbestos Mineral*, references as outlined in 6.1.

7.34 *Asbestos Standards*, as outlined in 3.1.2.

7.35 *Tygon[7] Tubing*, or equivalent.

7.36 *Small Vacuum Pump*, that can maintain a pressure of 92 kPa.

7.37 *Petri Dishes*, large glass, approximately 90 mm in diameter.

7.38 *Jaffe Washer*, stainless steel or aluminum mesh screen, 30 to 40 mesh, and approximately 75 mm by 50 mm in size.

7.39 *Copper TEM Finder Grids*, 200 mesh.

7.40 *Carbon Evaporator Rods.*

7.41 *Lens Tissue.*

7.42 *Ashless Filter Paper Filters*, 90 mm diameter.

7.43 *Gummed Paper Reinforcement Rings.*

7.44 *Wash Bottles*, plastic.

7.45 *Reagent Alcohol*, HPLC Grade (Fisher A995 or equivalent).

7.46 *Opening Mesh Screen*, plastic, 1.0 by 1.0 mm, (Spectra-Mesh #146410 or equivalent).

7.47 *Diffraction Grating Replica.*

8. Sampling Procedure for Microvacuum Technique

8.1 For sampling asbestos-containing dust in either indoor or outdoor environments, commercially available cassettes must be used. Air monitoring cassettes containing 25 mm or 37 mm diameter mixed cellulose ester (MCE) or polycarbonate (PC) filter membranes with a pore size less than or equal to 0.8 µm are required (7.31). The number of samples collected depends upon the specific circumstances of the study.

8.2 Maintain a log of all pertinent sampling information and sampling locations.

8.3 Sampling pumps and flow indicators shall be calibrated using a certified standard apparatus or assembly (see Practice D 3195 and 7.29).

8.4 Record all calibration information (5).

8.5 Perform a leak check of the sampling system at each sampling site by activating the pump (7.29) with the closed sampling cassette in line. Any air flow shows that a leak is present that must be eliminated before initiating the sampling operation.

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[6] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[7] Tygon is a registered trademark of the DuPont Co.

8.6 Attach the sampling cassette to the sampling pump at the outlet side of the cassette with plastic tubing (7.35). The plastic tubing must be long enough in that the sample areas can be reached without interference from the sampling pump. Attach a clean, approximately 25.4 mm long piece of plastic tubing (6.35 mm internal diameter) directly to the inlet orifice. Use this piece of tubing as the sampling nozzle. Cut the sampling end of the tubing at a 45° angle as illustrated in Fig. 1. The exact design of the nozzle is not critical as long as some vacuum break is provided to avoid simply pushing the dust around on the surface with the nozzle rather than vacuuming it into the cassette. The internal diameter of the nozzle and flow rate of the pump may vary as long as the air velocity is 100 (±10) cm/s. This air velocity calculation is based on an internal sampling tube diameter of 6.35 mm at a flow rate of 2 L/min.

8.7 Measure and determine the sample area of interest. A sample area of 100 cm^2 is vacuumed until there is no visible dust or particulates matter remaining. Perform a minimum of two orthogonal passes on the surface within a minimum of 2 min of sampling time. Avoid scraping or abrading the surface being sampled. (Do not sample any debris or dust particles greater than 1 mm in diameter (see 4.2).) Smaller or larger areas can be sampled, if needed. For example, some surfaces of interest may have a smaller area than 100 cm^2. Less dusty surfaces may require vacuuming of larger areas. Unlike air samples, the overloading of the cassettes with dust will not be a problem. As defined in 3.2.5, only dust shall be collected for this analysis.

8.8 At the end of sample collection, invert the cassette so that the nozzle inlet faces up before shutting off the power to the pump. The nozzle is then sealed with a cassette end-plug and the cassette/nozzle taped or appropriately packaged to prevent separation of the nozzle and cassette assembly. A second option is the removal of the nozzle from the cassette, then plugging of the cassette and shipment of the nozzle (also plugged at both ends) sealed in a separate closeable plastic bag. A third option is placing the nozzle inside the cassette for shipment. The nozzle is always saved and rinsed because a significant percentage of the dust drawn from a lightly loaded surface may adhere to the inside walls of the tubing.

8.9 Check that all samples are clearly labeled, that all dust sampling information sheets are completed, and that all perti-nent information has been enclosed, in accordance with laboratory quality control practices, before transfer of the samples to the laboratory. Include an unused cassette and nozzle as a field blank.

8.10 Wipe off the exterior surface of the cassettes with disposable wet towels (baby wipes) prior to packaging for shipment.

9. Sample Shipment

9.1 Ship dust samples to an analytical laboratory in a sealed container, but separate from any bulk or air samples. The cassettes must be tightly sealed and packed in a material free of fibers or dust to minimize the potential for contamination. Plastic "bubble pack" is probably the most appropriate material for this purpose.

10. Sample Preparation

10.1 Under a negative flow HEPA hood (7.5), carefully wet-wipe the exterior of the cassettes to remove any possible contamination before taking cassettes into a clean preparation area.

10.2 Perform sample preparation in a clean facility that has a separate work area from both the bulk and air sample preparation areas.

10.3 Initial specimen preparation shall take place in a clean HEPA filtered negative pressure hood to avoid any possible contamination of the laboratory or personnel, or both, by the potentially large number of asbestos structures in an asbestos-containing dust sample. Cleanliness of the preparation area hoods is measured by the cumulative process blank surface loadings (see Section 11).

10.4 All sample preparation steps 10.4.1-10.4.6 shall take place in the dust preparation area inside a HEPA hood.

10.4.1 Remove the upper plug from the sample cassette and carefully introduce approximately 10 mL solution of a 50/50 mixture of particle-free water and reagent alcohol into the cassette using a plastic wash bottle (7.44). If the plugged nozzle was left attached to the cassette, then remove the plug and introduce the water/alcohol solution into the cassette through the tubing, and then remove the tubing, if it is visibly clean.
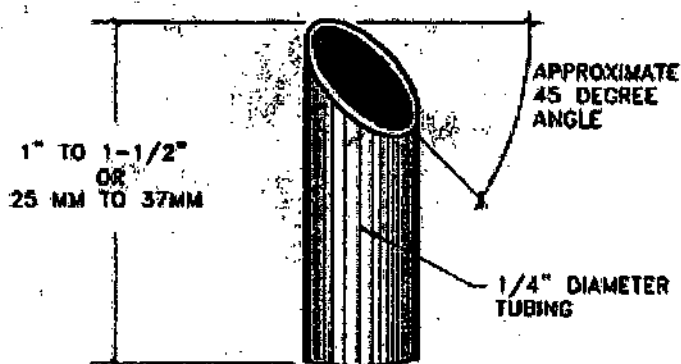

FIG. 1 Example of the Tubing Nozzle

1" TO 1-1/2"
OR
25 MM TO 37MM

APPROXIMATE 45 DEGREE ANGLE

1/4" DIAMETER TUBING

10.4.2 Replace the upper plug or the sample cap and lightly shake the dust solution by hand for 3 s.

10.4.3 Remove the entire cap of the cassette and pour the suspension through a 1.0 by 1.0 mm opening screen (7.46) into a pre-cleaned 200 mL glass specimen bottle (7.9). All visible traces of the sample contained in the cassette shall be rinsed through the screen into the specimen bottle with a plastic wash bottle containing the 50/50 solution of particle-free water and alcohol. Repeat this procedure two additional times for a total of three washings. Next, rinse the nozzle two or three times through the screen into the specimen bottle with the 50/50 mixture of water and alcohol. Typically, the total amount of the 50/50 mixture used in the rinse is 50 to 75 mL. Discard the 1.0 by 1.0 mm screen and bring the volume of suspension in the specimen bottle up to the 100 mL mark on the side of the bottle with particle-free water only.

10.4.4 Adjust the pH of the suspension to 3 to 4 using a 10.0 % solution of acetic acid. Use pH paper for testing. Filter the suspension within 24 h to avoid problems associated with bacterial and fungal growth.

10.4.5 Use either a disposable plastic filtration unit or a glass filtering unit (7.14) for filtration of aliquots of the suspension. The ability of an individual filtration unit to produce a uniform distribution may be tested by the filtration of a colored particulate solution such as diluted India ink (solution of carbon black).

10.4.5.1 If a disposable plastic filtration unit is used, then unwrap a new disposable plastic filter funnel unit (either 25 or 47 mm diameter) and remove the tape around the base of the funnel. Remove the funnel and discard the top filter supplied with the apparatus, retaining the coarse polypropylene support pad in place. Assemble the unit with the adapter and a properly sized neoprene stopper, and attach the funnel to the 1000 mL side-arm vacuum flask (7.15). Place a 5.0 µ m pore size MCE (backing filter) on the support pad. Wet it with a few mL of particle-free water and place an MCE (7.16) or PC filter (≤0.22 µm pore size) (7.17) on top of the backing filter. Apply a vacuum (7.36), ensuring that the filters are centered and pulled flat without air bubbles. Any irregularities on the filter surface requires the discard of that filter. After the filter has been seated properly, replace the funnel and reseal it with the tape. Return the flask to atmospheric pressure.

10.4.5.2 If a glass filtration unit is used, place a 5 µm pore size MCE (backing filter) on the glass frit surface. Wet the filter with particle-free water, and place an MCE or PC filter (≤0.22 µm pore size) on top of the backing filter. Apply a vacuum, ensuring that the filters are centered and pulled flat without air bubbles. Replace the filters if any irregularities are seen on the filter surface. Before filtration of each set of sample aliquots, prepare a blank filter by filtration of 50 mL of particle-free water. If aliquots of the same sample are filtered in order of increasing surface loading, the glass filtration unit need not be washed between filtration. After completion of the filtration, do not allow the filtration funnel assembly to dry because contamination is then more difficult to remove. Wash any residual solution from the filtration assembly by holding it under a flow of water, then rub the surface with a clean paper towel soaked

in a detergent solution. Repeat the cleaning operation, and then rinse two times in particle-free water.

10.4.6 With the flask at atmospheric pressure, add 20 mL of particle-free water into the funnel. Cover the filter funnel with its plastic cover if the disposable filtering unit is used.

10.4.7 Briefly hand shake (3 s) the capped bottle with the sample suspension, then place it in a tabletop ultrasonic bath (7.12) and sonicate for 3.0 min. Maintain the water level in the sonicator at the same height as the suspension in sample bottle. The ultrasonic bath shall be calibrated as described in 20.5. The ultrasonic bath must be operated at equilibrium temperature. After sonicating, return the sample bottle to the work surface of the HEPA hood. Preparation steps 10.4.8-10.4.14 shall be carried out in this hood.

10.4.8 Shake the suspension lightly by hand for 3 s, then let it rest for 2.0 min to allow large particles to settle to the bottom of the bottle or float to the surface.

10.4.9 Estimate the amount of liquid to be withdrawn to produce an adequate filter preparation. Experience has shown that a light staining of the filter surface will yield a suitable preparation for analysis. Filter at least 1.0 mL, but no more than half the total volume. If after examination in the TEM, the smallest volume measured (1.0 mL) (7.13) yields an overloaded sample, then perform additional serial dilutions of the suspension. If it is estimated that less than 1.0 mL of suspension has to be filtered because of the density of the suspension, perform a serial dilution.

10.4.9.1 If serial dilutions are required, repeat step 10.4.8 before the serial dilution portion is taken. Do not re-sonicate the original suspension or any serial dilutions. The recommended procedure for a serial dilution is to mix 10 mL of the sample suspension with 90 mL of particle-free water in a clean sample bottle to obtain a 1:10 serial dilution. Follow good laboratory practices when performing dilutions.

10.4.10 Insert a new disposable pipette halfway into the sample suspension and withdraw a portion. Avoid pipetting any of the large floating or settled particles. Uncover the filter funnel and dispense the mixture from the pipette into the water in the funnel.

10.4.11 Apply vacuum to the flask and draw the mixture through the filter.

10.4.12 Discard the pipette.

10.4.13 Disassemble the filtering unit and carefully remove the sample filter with fine tweezers (7.11). Place the completed sample filter particle side up, into a precleaned, labeled, disposable, plastic petri dish (7.48) or other similar container.

10.4.14 In order to ensure that an optimally-loaded filter is obtained, it is recommended that filters be prepared from several different aliquots of the dust suspension. For this series of filters, it is recommended that the volume of each aliquot of the original suspension be a factor of five higher than the previous one. If the filters are prepared in order of increasing aliquot volume, all of the filters for one sample can be prepared using one plastic disposable filtration unit, or without cleaning of glass filtration equipment between individual filtration. Before withdrawal of each aliquot from the sample, shake the suspension without additional sonification and allow to rest for 2 min.

10.4.15 There are many practical methods for drying MCE filters. The following are two examples that can be used: (*1*) dry MCE filters for at least 12 h (over desiccant) in an airtight cabinet-type desiccator (7.21); (2) to shorten the drying time (if desired), remove a plug of the damp filter and attach it to a glass slide (7.19) as described in 12.1.2 and 12.1.3. Place the slide with a filter plug or filter plugs (up to eight plugs can be attached to one slide) on a bed of desiccant, in the desiccator for 1 h.

10.4.16 PC filters do not require lengthy drying before preparation, but shall be placed in a desiccator for at least 30 min before preparation.

10.5 Prepare TEM specimens from small sections of each dried filter using the appropriate direct transfer preparation method.

11. Blanks

11.1 Prepare sample blanks that include both a process blank (50 mL of particle-free water) for each set of samples analyzed and one unused filter from each new box of sample filters (MCE or PC) used in the laboratory. If glass filtering units are used, prepare and analyze a process blank each time the filtering unit is cleaned. Blanks will be considered contaminated, if after analysis, they are shown to contain more than 53 asbestos structures per square millimetre. This generally corresponds to three or four asbestos structures found in ten grid openings. The source of the contamination must be found before any further analysis can be performed. Reject samples that were processed along with the contaminated blanks and prepare new samples after the source of the contamination is found.

11.2 Prepare field blanks which are included with sample sets in the same manner as the samples, to test for contamination during the sampling, shipping, handling, and preparation steps of the method.

12. TEM Specimen Preparation of Mixed Cellulose Ester (MCE) Filters

Note 1—Use of either the acetone or the diamethylformamide-acetic acid method is acceptable.

12.1 *Acetone Fusing Method:*

12.1.1 Remove a section (a plug) from any quadrant of the sample and blank filters. Sections can be removed from the filters using a 7 mm cork borer (7.32). The cork borer must be wet wiped after each time a section is removed.

12.1.2 Place the filter section (particle side up) on a clean microscope slide. Affix the filter section to the slide with a gummed page reinforcement (7.43), or other suitable means. Label the slide with a glass scribing tool or permanent marker (7.10).

12.1.3 Prepare a fusing dish from a glass petri dish (7.37) and a metal screen bridge (7.38) with a pad of five to six ashless paper filters (7.42) and place in the bottom of the petri dish (4). Place the screen bridge on top of the pad and saturate the filter pads with acetone. Place the slide on top of the bridge in the petri dish and cover the dish. Wait approximately 5 min for the sample filter to fuse and clear.

12.2 *Dimethylformamide-Acetic Acid Method:*

12.2.1 Place a drop of clearing solution that consists of 35 % dimethylformamide (DMF), 15 % glacial acetic acid, and 50 % Type II water (v/v) on a clean microscope slide. Gauge the amount used so that the clearing solution just saturates the filter section.

12.2.2 Carefully lay the filter segment, sample surface upward, on top of the solution. Bring the filter and solution together at an angle of about 20° to help exclude air bubbles. Remove any excess clearing solution. Place the slide in an oven or on a hot plate, in a fume hood, at 65 to 70°C for 10 min.

12.3 Plasma etching of the collapsed filter is required.

12.3.1 The microscope slide to which the collapsed filter pieces are attached is placed in a plasma asher (7.27). Because plasma ashers vary greatly in their performance, both from unit to unit and between different positions in the asher chamber, it is difficult to specify the exact conditions that must be used. Insufficient etching will result in a failure to expose embedded fibers, and too much etching may result in the loss of particles from the filter surface. To determine the optimum time for ashing, place an unused 25 mm diameter MCE filter in the center of a glass microscope slide. Position the slide approximately in the center of the asher chamber. Close the chamber and evacuate to a pressure of approximately 40 Pa, while admitting oxygen to the chamber at a rate of 8 to 20 cm³/min. Adjust the tuning of the system so that the intensity of the plasma is maximized. Determine the time required for complete oxidation of the filter. Adjust the system parameters to achieve complete oxidation of the filter in a period of approximately 15 min. For etching of collapsed filters, use these operating parameters for a period of 8 min. For additional information on calibration, see the *USEPA Asbestos-Containing Materials in Schools* (4) or *NIST/NVLAP Program Handbook for Airborne Asbestos Analysis* (6) documents.

12.3.2 Place the glass slide containing the collapsed filters into the low-temperature plasma asher, and etch the filter.

12.4 Carbon coating of the collapsed and etched filters is required.

12.4.1 Carbon coating must be performed with a high-vacuum coating unit (7.4), capable of less than 10^{-4} torr (13 MPa) pressure. Units that are based on evaporation of carbon filaments in a vacuum generated only by an oil rotary pump have not been evaluated for this application and shall not be used. Carbon rods (7.40) used for evaporators shall be sharpened with a carbon rod sharpener to a neck of about 4 mm in length and 1 mm in diameter. The rods are installed in the evaporator in such a manner that the points are approximately 100 to 120 mm from the surface of the microscope slide held in the rotating device.

12.4.2 Place the glass slide holding the filters on the rotation device, and evacuate the evaporator chamber to a vacuum of at least 13 MPa. Perform the evaporation in very short bursts, separated by 3 to 4 s to allow the electrodes to cool. An alternate method of evaporation is by using a slow continuous applied current. An experienced analyst can judge the thickness of the carbon film to be applied. Conduct tests on unused filters first. If the carbon film is too thin, large particles will be lost

from the TEM specimen, and there will be few complete and undamaged grid openings on the specimen.

12.4.2.1 If the coating is too thick, it will lead to a TEM image that is lacking in contrast, and the ability to obtain electron diffraction patterns will be compromised. The carbon film shall be as thin as possible and still remain intact on most of the grid openings of the TEM specimen.

12.5 *Preparation of the Jaffe Washer*— The precise design of the Jaffe washer is not considered important, so any one of the published designs may be used (7, 8). One such washer consists of a simple stainless steel bridge contained in a glass petri dish.

12.5.1 Place several pieces of lens tissue (7.41) on the stainless steel bridge. The pieces of lens tissue shall be large enough to completely drape over the bridge and into the solvent. In a fume hood, fill the petri dish with acetone (or DMF) until the height of the solvent is brought up to contact the underside of the metal bridge as illustrated in Fig. 2.

12.6 *Placing the Specimens into the Jaffe Washer:*

12.6.1 Place the TEM grids (7.39) shiny side up on a piece of lens tissue or filter paper so that individual grids can be easily picked up with tweezers.

12.6.2 Prepare three grids from each sample.

12.6.2.1 Using a curved scalpel blade (7.20), excise at least two square (3 mm by 3 mm) pieces of the carbon-coated MCE filter from the glass slide.

12.6.2.2 Place the square filter piece carbon-side up on top of a TEM specimen grid.

12.6.2.3 Place the whole assembly (filter/grid) on the saturated lens tissue in the Jaffe washer.

12.6.2.4 Place the three TEM grid sample filter preparations on the same piece of lens tissue in the Jaffe washer.

12.6.2.5 Place the lid on the Jaffe washer and allow the system to stand for several hours.

12.7 Alternately, place the grids on a low level (petri dish filled to the ⅛ mark) DMF Jaffe washer for 60 min. Add enough solution of equal parts DMF/acetone to fill the washer to the screen level. Remove the grids after 30 min if they have cleared, that is, all filter material has been removed from the carbon film, as determined by inspection in the TEM.

12.8 Carefully remove the grids from the Jaffe washer, allowing the grids to dry before placing them in a clean marked grid box.
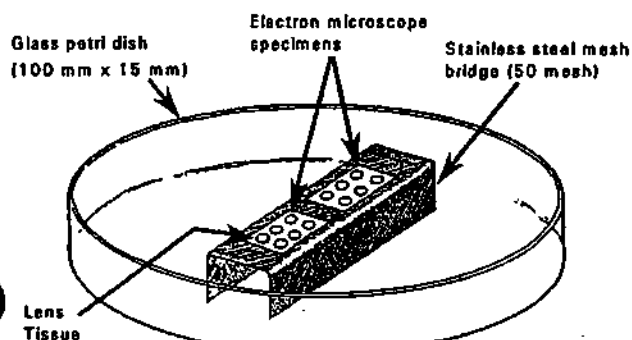

FIG. 2 Example of Design of Solvent Washer (Jaffe Washer)

13. TEM Specimen Preparation of Polycarbonate (PC) Filter

13.1 Cover the surface of a clean microscope slide with two strips of double-sided adhesive tape.

13.2 Cut a strip of filter paper slightly narrower than the width of the slide. Position the filter paper strip on the center of the length of the slide.

13.3 Using a clean, curved scalpel blade, cut a strip of the PC filter approximately 25 by 6 mm. Use a rocking motion of the scalpel blade to avoid tearing the filter. Place the PC strip particle side up on the slide perpendicular to the long axis of the slide. The ends of the PC strip must contact the double sided adhesive tape. Each slide can hold several PC strips. With a glass marker, label each PC strip with the individual sample number.

13.4 Carbon coat the PC filter strips as discussed in 12.4.2. PC filters do not require etching.

NOTE 2—Caution: Do not overheat the filter sections while carbon coating.

13.5 Prepare a Jaffe washer as described in 12.5, but fill the washer with chloroform or 1-methyl-2-pyrrolidone to the level of the screen.

13.6 Using a clean curved scalpel blade, excise three, 3-mm square filter pieces from each PC strip. Place the filter squares carbon side up on the shiny side of a TEM grid. Pick up the grid and filter section together and place them on the lens tissue in the Jaffe washer.

13.7 Place the lid on the Jaffe washer and rest the grids in place for at least 4 h. Best results are obtained with longer wicking times, up to 12 h.

13.8 Carefully remove the grids from the Jaffe washer, allowing the grids to dry before placing them in a clean, marked grid box.

14. Grid Opening Measurements

14.1 TEM grids must have a known grid opening area. Determine this area as follows:

14.2 Measure at least 20 grid openings in each of 20 random 75 to 100 μm (200-mesh) copper grids for a total of 400 grid openings for every 1000 grids used, by placing the 20 grids on a glass slide and examining them under the optical microscope. Use a calibrated graticule to measure the average length and width of the 20 openings from each of the individual grids. From the accumulated data, calculate the average grid opening area of the 400 openings.

14.3 Grid area measurements can also be made at the TEM at a calibrated screen magnification of between 15 000 and 20 000X. Typically measure one grid opening for each grid examined. Measure grid openings in both the x and y directions and calculate the area.

14.4 Pre-calibrated TEM grids are also acceptable for this test method.

15. TEM Method

15.1 Microscope settings: 80 to 120 kV, 15 000 to 20 000X screen magnification for analysis (7.2).

15.2 Analyze two grids for each sample. Analyze one-half of the sample area on one sample grid preparation and the remaining half on a second sample grid preparation.

15.3 *Determination of Specimen Suitability:*

15.3.1 Carefully load the TEM grid, carbon side facing up (in the TEM column) with the grid bars oriented parallel/perpendicular to the length of the specimen holder. Use a hand lens or loupe, if necessary. This procedure will line up the grid with the *x* and *y* translation directions of the microscope. Insert the specimen holder into the microscope.

15.3.2 Scan the entire grid at low magnification (250X to 1000X) to determine its suitability for high magnification analysis as specified in 15.3.3.

15.3.3 Grids are acceptable for analysis if the following conditions are met:

15.3.3.1 The fraction of grid openings covered by the replica section is at least 50 %.

15.3.3.2 Relative to that section of the grid covered by the carbon replica, the fraction of intact grid openings is greater than 50 %.

15.3.3.3 The fractional area of undissolved filter is less than 10 %.

15.3.3.4 The fraction of grid openings with overlapping or folded replica film is less than 50 %.

15.3.3.5 At least 20 grid openings, that have no overlapping or folded replica, are less than 5 % covered with holes and have less than 5 % opaque area due to incomplete filter dissolution.

15.4 *Determination of Grid Opening Suitability:*

15.4.1 If the grid meets acceptance criteria, choose a grid opening for analysis from various areas of the grid so that the entire grid is represented. Determine the suitability of each individual grid opening prior to the analysis.

15.4.2 The individual grid opening must have less than 5 % holes over its area.

15.4.3 Grid openings must be less than 25 % covered with particulate matter.

15.4.4 Grid openings must be uniformly loaded.

15.5 Observe and record the orientation of the grid at 80 to 150X, on a grid map record sheet along with the location of the grid openings that are examined for the analysis. If indexed grids are used, a grid map is not required, but the identifying coordinates of the grid square must be recorded.

16. Recording Data Rules

16.1 Record on the count sheet any continuous grouping of particles in which an asbestos fiber is detected. Classify asbestos structures as fibers, bundles, clusters, or matrices as defined in 5.2.

16.2 Use the criteria for fiber, bundle, cluster, and matrix identification, as described in the *USEPA Asbestos-Containing Materials in Schools* document (4). Record, for each AHERA structure identified, the length and width measurements.

16.3 Record NSD (No Structures Detected) when no structures are detected in the grid opening.

16.4 Identify structures classified as chrysotile identified by either electron diffraction or X-ray analysis (7.3) and recorded on a count sheet. Verify at least one out of every ten chrysotile structures by X-ray analysis.

16.5 Structures classified as amphiboles by X-ray analysis and electron diffraction are recorded on the count sheet. For more information on identification, see Yamate, et al, (7) or Chatfield and Dillon (8).

16.6 Record a typical electron diffraction pattern for each type of asbestos observed for each group of samples (or a minimum of every five samples) analyzed. Record the micrograph number on the count sheet. Record at least one X-ray spectrum for each type of asbestos observed per sample. Attach the print-outs to the back of the count sheet. If the X-ray spectrum is stored, record the file and disk number on the count sheet.

16.7 *Counting Rules:*

16.7.1 At a screen magnification of between 15 000 and 20 000X evaluate the grids for the most concentrated sample loading; reject the sample if it is estimated to contain more than 50 asbestos structures per grid opening. Proceed to the next lower concentrated sample until a set of grids are obtained that have less than 30 asbestos structures per grid opening.

16.8 *Analytical Sensitivity (AS)*—As determined by the following equation:

$$(EFA \times 100\ mL \times 1)/(GO \times GOA \times V \times SPL) = AS \qquad (1)$$

where:
EFA = effective filter area of the final sampling filter, mm^2
GO = number of grid openings counted
GOA = average grid opening area, mm^2
SPL = surface area sampled, cm^2
V = volume of sample filtered in step 10.4.9, representing the actual volume taken from the original 100 mL suspension, mL
AS = analytical sensitivity, expressed as asbestos structures/cm^2

16.8.1 An AS of approximately 1000 asbestos structures per square centimetre (calculated for the detection of a single asbestos structure) has been designed for this analysis. This sensitivity can be achieved by increasing the amount of liquid filtered, increasing the number of grid openings analyzed, increasing the area of the collection, or decreasing the size of the final filter. For example, using a collection area = 500 cm^2, filter area = 1000 mm^2, number of grid openings = 10, and a grid area of 0.01 mm^2, V = 50 mL, the AS is 40 str/cm^2. Occasionally, due to high particle loadings or high asbestos surface loading, this AS cannot be practically achieved and stopping rules apply.

16.8.2 The numerical value of AS required for any specific application of this method may be achieved by selecting an appropriate combination of the sampling and analysis parameters in the above equation. For example, if SPL = 100 cm^2, EFA = 1000 mm^2, GO = 10, GOA = 0.01 mm^2, V = 10 mL, and D = 1, then AS = 1000 str/cm^2. Increasing GO to 50 and V to 50 mL changes the AS to 40 Str/cm^2.

16.8.3 When sample filters are heavily loaded with particulate matter, it may useful to employ serial dilutions during preparation to reduce the loading on grid specimens to acceptable levels and thus facilitate analysis. Under such circumstances, the AS may be calculated by substituting an appropriate value for the dilution factor, D, into the above equation. In general:

8

$$D = VA/(V + VPFW) \qquad (2)$$

VA = the volume of the aliquot from the new, diluted suspension that is filtered to prepare the analytical filter; V = the volume of the aliquot from the initial (100 mL) suspension that is diluted; and VPFW = the volume of particle free water added to V during serial dilution to produce the new, diluted suspension.

Thus, if GO = 10, V = 10 mL, VPFW = 90 mL, and VA = 1.0 mL, D = 0.01 and the AS = 100 000 str/cm^2.

16.9 *Limit of Detection*—The limit of detection for this test method is calculated using the Practice D 6620. All data shall be provided in the laboratory report.

16.10 *Stopping Rules*:

16.10.1 The analysis is stopped upon the completion of the grid square that achieves an AS of less than 1000 asbestos structures per square centimetre.

16.10.2 If an AS of 1000 asbestos structures per square centimetre cannot be achieved after analyzing ten grid openings then stop on grid opening No. 10 or the grid opening which contains the 100th asbestos structure, whichever comes first. A minimum of four grid squares shall be analyzed for each sample.

16.10.2.1 If the analysis is stopped because of the 100th structure rule, the entire grid square containing the 100th structure must be counted.

16.11 After analysis, remove the grids from the TEM, and replace them in the appropriate grid storage holder.

17. Sample Storage

17.1 The washed-out sample cassettes can be discarded after use.

17.2 Sample grids and unused filter sections (7.18) must be stored for a minimum of one year.

18. Reporting

18.1 Report the following information for each dust sample analyzed:

18.1.1 Surface loading in structures/cm^2.

18.1.2 The AS.

18.1.3 Types of asbestos present.

18.1.4 Number of asbestos structures counted.

18.1.5 Effective filtration area.

18.1.6 Average size of the TEM grid openings that were counted.

18.1.7 Number of grid openings examined.

18.1.8 Sample dilution used.

18.1.9 Area of the surface sampled.

18.1.10 Listing of size data for each structure counted.

18.1.11 A copy of the TEM count sheet or a complete listing of the raw data. An example of a typical count sheet is shown in Appendix X1.

18.2 Determine the amount of asbestos in any accepted sample using the following formula:

$$\frac{EFA \times 100 \text{ mL} \times \#STR}{GO \times GOA \times V \times SPL} = \text{asbestos structures/cm}^2 \qquad (3)$$

where:

#STR = number of asbestos structures counted,
EFA = effective filter area of the final sampling filter, mm^2,
GO = number of grid openings counted,
GOA = average grid opening area, mm^2,
SPL = surface area sampled, cm^2, and
V = volume of sample filtered in step 10.4.9, representing the actual volume taken from the original 100 mL suspension, mL.

19. Quality Control/Quality Assurance

19.1 In general, the laboratory's quality control checks are used to verify that a system is performing according to specifications regarding accuracy and consistency. In an analytical laboratory, spiked or known quantitative samples are normally used. However, due to the difficulties in preparing known quantitative asbestos samples, routine quality control testing focuses on re-analysis of samples (duplicate recounts).

19.1.1 Re-analyze samples at a rate of $\frac{1}{10}$ of the sample sets (one out of every ten samples analyzed not including laboratory blanks). The re-analysis shall consist of a second sample preparation obtained from the final filter.

19.2 In addition, quality assurance programs must follow the criteria shown in the *USEPA Asbestos-Containing Materials in Schools* document (4) and in the *NIST/NVLAP Program Handbook for Airborne Asbestos Analysis* document (6). These documents describe sample custody, sample preparation, blank checks for contamination, calibration, sample analysis, analyst qualifications, and technical facilities.

20. Calibrations

20.1 Perform calibrations of the instrumentation on a regular basis, and retain these records in the laboratory, in accordance with the laboratory's quality assurance program.

20.2 Record calibrations in a log book along with dates of calibration and the attached backup documentation.

20.3 A calibration list for the instrument is as follows:

20.3.1 *TEM*:

20.3.1.1 Check the alignment and the systems operation. Refer to the TEM manufacturer's operational manual for detailed instructions.

20.3.1.2 Calibrate the camera length of the TEM in electron diffraction (ED) operating mode before ED patterns of unknown samples are observed. Camera length can be measured by using a carbon coated grid on which a thin film of gold has been sputtered or evaporated. A thin film of gold is evaporated on the specimen TEM grid to obtain zone-axis ED patterns superimposed with a ring pattern from the polycrystalline gold film. In practice, it is desirable to optimize the thickness of the gold film so that only one or two sharp rings are obtained on the superimposed ED pattern. Thick gold films will tend to mask weak diffraction spots from the fibrous particles. Since the unknown d-spacings of most interest in asbestos analysis are those which lie closest to the transmitted beam, multiple gold rings from thick films are unnecessary. Alternatively, a gold standard specimen can be used to obtain an average camera constant calculated for that particular instrument and can then be used for ED patterns of unknowns taken during the corresponding period.

20.3.1.3 Perform magnification calibration at the fluorescent screen. This calibration must be performed at the magnification used for structure counting. Calibration is performed with a grating replica (7.47) (for example, one containing at least 2160 lines/mm).

(a) Define a field of view on the fluorescent screen. The field of view must be measurable or previously inscribed with a scale or concentric circles (all scales should be metric).

(b) Frequency of calibration will depend on the service history of the particular microscope.

(c) Check the calibration after any maintenance of the microscope that involves adjustment of the power supply to the lens or the high voltage system or the mechanical disassembly of the electron optical column (apart from filament exchange).

(d) The analyst must ensure that the grating replica is placed at the same distance from the objective lens as the specimen.

(e) For instruments that incorporate a eucentric tilting specimen stage, all specimens and the grating replica must be placed at the eucentric position.

20.3.1.4 The smallest spot size of the TEM must be checked.

(a) At the crossover point, photograph the spot size at a screen magnification of 15 000 to 20 000X. An exposure time of 1 s is usually adequate.

(b) The measured spot size must be less than or equal to 250 nm.

20.4 *EDXA:*

20.4.1 The resolution and calibration of the EDXA must be verified.

20.4.1.1 Collect a standard EDXA Cu peak from the Cu grid.

20.4.1.2 Compare the X-ray energy versus channel number for the Cu peak and be certain that readings are within ±10 eV.

20.4.2 Collect a standard EDXA of crocidolite asbestos (NIST SRM 1866).

20.4.2.1 The elemental analysis of the crocidolite must resolve the Na peak.

20.4.3 Collect a standard EDXA of chrysotile asbestos.

20.4.3.1 The elemental analysis of chrysotile must resolve both Si and Mg on a single chrysotile fiber.

20.5 Ultrasonic bath calibration shall be performed as follows:

20.5.1 Fill the bath water to a level equal to the height of suspension in the glass sample container that will be used for the dust analysis. Operate the bath until the water reaches the equilibrium temperature.

20.5.2 Place 100 mL of water (at approximately 20°C) in another 200-mL glass sample container, and record its temperature.

20.5.3 Place the sample container in the water in the ultrasonic bath (with the power turned off). After 60 s, remove the glass container and record its temperature.

20.5.4 Place 100 mL of water (at approximately 20°C) in another 200-mL glass sample container, and record its temperature.

20.5.5 Place the second sample container into the water in the ultrasonic bath (with the power turned on). After 60 s, remove the glass container and record its temperature.

20.5.6 Calculate the rate of energy deposition into the sample container using the following formula:

$$R = 4.185 \times \sigma \times \rho \times \frac{(\theta_2 - \theta_1)}{t} \qquad (4)$$

where:
4.185 = Joules/cal,
R = energy deposition, watts/mL,
θ_1 = temperature rise with the ultrasonic bath not operating, °C,
θ_2 = temperature rise with the ultrasonic bath operating, °C.
t = time in seconds, 60 s (20.5.3 and 20.5.5),
σ = specific heat of the liquid in the glass sample container, 1.0 cal/g, and
ρ = density of the liquid in the glass sample container, 1.0 g/cm^3.

20.5.7 Adjust the operating conditions of the bath so that the rate of energy deposition is in the range of 0.08 to 0.12 MW/m³, as defined by this procedure.

21. Precision and Bias

21.1 *Precision*—The precision of the procedure in this test method is being determined using round robin data from participating laboratories.

21.2 *Bias*—Since there is no accepted reference material suitable for determining the bias of the procedure in this test method, bias has not been determined (see Specification D 3670).

NOTE 3—Round robin data is under development and will be presented as a research report.

22. Keywords

22.1 asbestos; microvacuuming; settled dust; TEM

APPENDIX

(Nonmandatory Information)

X1. DUST SAMPLE ANALYSIS

X1.1   See Figs. X1.1 and X1.2 for the dust analysis worksheet and the TEM count sheet.

DUST SAMPLE ANALYSIS

Client: _____

Accelerating Voltage: _____

Sample ID: _____

Indicated Mag: _____ KX

Job Number: _____

Screen Mag: _____ KX

Date Sample Analyzed: ___ - ___ - ___

Microscope: 1   2   3   4   5

Number of Openings/Grids Counted: _____|

Filter Type: _____

Grid Accepted, 600X: Yes   No

Filter Size: _____

Percent Loading: _____ %

Filter Pore Size (μm): _____

Grid Box #1: _____

Grid Opening: 1) _____ μm x _____ μm

2) _____ μm x _____ μm

Analyst: _____

Reviewer: _____

Counting Rules: AHERA   LEVEL II

Calculation Data:

Effective Filter Area in mm^2: (EFA) _____

Number of Grid Openings Counted: (GO) _____

Average Grid Opening Area in mm^2: (GOA) _____

Volume of sample Filtered in ml: (V) _____

Surface area Sampled in cm^2: (SPL) _____

Number of Asbestos Structures Counted:* (#STR) _____

* If the number of asbestos structures counted is less than or equal to 4, enter 4 structures as the limit of detection here.

FORMULA FOR CALCULATION OF ASBESTOS STRUCTURES "DUST" PER CM^2:

$$\frac{EFA\ X\ 100\ X\ \#STR}{GO\ X\ GOA\ X\ VX\ SPL} = \text{(Asbestos Structures per cm}^2\text{)}$$

Results for Total Asbestos Structures: _____

(Structures per cm^2)

Results for Structures ≥ microns: _____

(Structures per cm^2)

FIG. X1.1 Dust Sample Analysis Work Sheet

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Job Number: _____

Structure #	Grid # Square #	Type	Structure	Length Microns	Width Microns	Confirmation		
						Morph.	SAED	EDS

Note: Keys to Abbreviations Used in Figure:

Type:

C	=	Chrysotile
AM	=	Amosite
CR	=	Crocidolite
AC	=	Actinolite
TR	=	Tremolite
AN	=	Anthophyllite
N	=	Non Asbestos

Structure:

F	=	Fiber
B	=	Bundle
C	=	Cluster
M	=	Matrix

Others:

NSD	=	No Structures Detected
Morph	=	Morphology
SAED	=	Selected Area Electron Diffraction
EDS	=	Energy Dispersive X-Ray Spectroscopy
ER	=	Inter-Row Spacing
NP	=	No Pattern

FIG. X1.2 TEM Count Sheet

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D 5755 – 03

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COLOR CHART(S)

THE FOLLOWING PAGES CONTAIN COLOR THAT DOES NOT APPEAR IN THE SCANNED IMAGES

To view the actual documents, please contact the Superfund Records Center at (303) 312-6473.

Amphibole (Asbestos) Minerals Refractive Index Comparisons

Scale: 1.590 1.600 1.610 1.620 1.630 1.640 1.650 1.660 1.670 1.680 1.690 1.700 1.710

Mineral		Values
Tremolite, Actinolite, Ferro Actinolite (Deer Howie & Zussman)[1]	α	1.599 – 1.688
	β	1.610 – 1.697
	γ	1.620 – 1.705
Tremolite (NIST)[2]	α	1.606
	β	~1.623
	γ	1.634
Tremolite (M°Crone)[3]	α	1.604 – 1.619
	β	1.617 – 1.632
	γ	1.627 – 1.642
Tremolite (Verkouteren/Wylie)[4]	α	1.599 – 1.612
	β	1.615 – 1.628
	γ	1.627 – 1.638
Predicted End Member Values Tremolite (Verkouteren/Wylie)[4]	α	~1.602
	β	~1.621
	γ	~1.631
Actinolite (NIST)[2]	α	1.613
	β	~1.629
	γ	1.639
Actinolite (Phillips/Griffin)[5]	α	1.620 – 1.670
	β	1.630 – 1.675
	γ	1.645 – 1.688
Actinolite (M°Crone)[3]	α	1.619 – 1.668
	β	1.632 – 1.675
	γ	1.642 – 1.688
Actinolite (Verkouteren/Wylie)[4]	α	1.611 – 1.639
	β	1.629 – 1.657
	γ	1.638 – 1.665
Actinolite (Deer Howie & Zussman)[1]	α	1.617 – 1.650
	β	1.630 – 1.663
	γ	1.640 – 1.670

Amphibole (Asbestos) Minerals Refractive Index Comparisons

Refractive index scale: 1.590 1.600 1.610 1.620 1.630 1.640 1.650 1.660 1.670 1.680 1.690 1.700 1.710

Mineral	Ray	Range
Ferro Actinolite (McCrone)[3]	α	1.668 – 1.684
	β	1.675 – 1.692
	γ	1.688 – 1.701
Ferro Actinolite (Verkouteren/Wylie)[4]	α	1.642 – 1.656
	β	1.661 – 1.678
	γ	1.670 – 1.687
Ferro Actinolite (Deer Howie & Zussman)[1]	α	1.642 – 1.668
	β	1.658 – 1.675
	γ	1.668 – 1.686
Predicted End Member Values Ferro Actinolite (Verkouteren/Wylie)[4]	α	~1.661
	β	~1.692
	γ	~1.700
Richterite, Ferro-Richterite (Deer Howie & Zussman)[1]	α	1.604 – 1.690
	β	1.616 – 1.700
	γ	1.622 – 1.712
Winchite [1,4,7]	α	←1.576 – 1.651
	β	1.628 – 1.655
	γ	1.590 – 1.671
Thesis Index Range (Bandli)[8]	α	1.618 – 1.627
	β	1.631 – 1.637
	γ	1.634 – 1.642

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Figure 2

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Reflectance Spectroscopy as a Rapid Assessment Tool for the Detection of Amphiboles from the Libby, Montana Region

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Introduction

The vermiculite mineral deposit near Libby, Montana was mined from the 1920's to 1990. During this period, the Libby mine was a major source of the nation's vermiculite, which was used in a variety of applications such as loose-fill insulation, additives to potting soil, packing materials for hazardous chemicals, and many others. Asbestiform amphiboles occur in veins throughout the deposit (e.g. Pardee and Larsen, 1929) and it is difficult to separate all asbestos from the vermiculite. This paper shows that the amphibole asbestos also occurs intergrown in the vermiculite, between the layers of the vermiculite sheet silicate.

The Asbestiform amphiboles from the Libby deposit have been linked to elevated occurrences of health problems in the Libby population (e.g. Amandus et al., 1987), including miners and mill workers exposed occupationally to dusts containing the amphiboles, as well as residents with no occupational exposures (Lybarger et al., 2001; Dearwent et al., 2000; McDonald et al., 1986). The town of Libby and the surrounding region are currently being evaluated by the U.S. Environmental Protection Agency (EPA) to assess the extent of potential asbestos contamination in buildings and soils. The EPA and its contractors have identified a region covering dozens of square miles in and around Libby to be assessed, which will require the collection of many thousands of samples to be analyzed for the potential presence of fibrous or asbestiform amphiboles.

Detection of asbestiform amphibole contamination can be difficult in certain situations. For example, in the case of Libby vermiculites, amphibole fibers can grow in between vermiculite layers (Figure 1). The index of refraction of vermiculite and the tremolite-richterite-winchite amphibole compositions found at Libby are nearly identical, thus normal optical microscopy methods will likely not be able to distinguish the presence of embedded amphiboles. Surface methods such as Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) do not probe into the vermiculite grains. In other cases, the fibers may be too small to easily detect with standard optical microscopy methods (OSHA Regulations Standards 29-CR, 1995). Finally, with so many samples needing characterization, a low cost, rapid method is needed to detect Libby amphiboles.

In this paper, we present the reflectance spectral properties of geologic materials from the Libby region and show how reflectance spectroscopy can be used as a rapid assessment tool. This report also discusses some limitations of this tool.

Figure 1. Richterite fibers that grew in between the layers of vermiculite/hydrobiotite in the Libby, MT deposit. This photo shows the light colored tremolite/richterite fibers after a book of vermiculite was split apart. The image is about 3.5 cm across.

Requirements of a Rapid Assessment Tool

A rapid assessment tool should be fast (measurements in minutes, with seconds desirable), require no sample preparation and be able to assess large volumes of material quickly with detection thresholds approximately constrained. Conditions of false negatives or positives should be known so that samples can be flagged for other analyses. The tool should reduce the workload of more expensive and longer analyses. Ideally, the tool could be easily deployed on site. A rapid assessment tool is not required to derive accurate abundances because detection above a threshold may be sufficient to identify samples containing the material of interest. If the methodology can flag sufficient numbers of samples, thereby reducing the number of samples needing analysis by other, longer and more expensive methods, then the use of rapid assessment strategy is warranted. This multi-level strategy we call the "Sieve" Strategy of Analyses (Figure 2).

An Asbestos Analysis Strategy

Desired Response	Example Method	Sample Accuracy	Sample Volume/Prep	Cost	Detection Speed
Real Time	Visual Assessment	Low	Large/none	Lowest	Fastest
Rapid	RS	Low/Medium	Large/none	Low	v. Fast
Rapid	PLM	Low/Medium	Low/yes	Low	Fast
Detailed	SEM, XRD	Medium/High	Low/yes	Medium	Slow
Definitive	TEM	High	v. Low/yes	High	v. Slow

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Figure 2. Different assessment strategies are shown. Each analysis has its own strengths, whether it is high accuracy or low cost, but no current analysis is rapid, very accurate and low cost. A reasonable approach is a combination of methods which can assess some samples quickly and at low cost, leaving fewer samples that need more expensive analyses. RS is Reflectance Spectroscopy, PLM is Polarized Light Microscopy;, SEM is Scanning Electron Microscopy, XRD is X-Ray Diffraction, and TEM is Transmission Electron Microscopy.

Reflectance Spectroscopy Background

Reflectance spectroscopy is a tool where electromagnetic radiation can be used to probe a surface and, through the absorption features in the spectrum of the scattered light, can be used to identify materials. Further, the sample needs no preparation, and with modern portable instruments, high quality reflectance spectra of a sample may be obtained in just a few seconds. Conditions of false negatives and false positives can be identified by a trained analyst. Accurate abundances are usually difficult to determine with reflectance spectroscopy, but approximate thresholds can be determined (e.g. see Clark and Roush, 1984; Clark 1999 and references therein). The characteristics of this methodology are therefore well suited for use as a rapid screening tool.

As photons enter a mineral, some are reflected from grain surfaces, some pass through the grain, and some are absorbed. Those photons that are reflected from grain surfaces or refracted through a particle are said to be scattered. Scattered photons may encounter another grain or be scattered away from the surface so they may be detected and measured. The more material the photons pass through, the greater the relative absorption feature strengths will appear in the observed spectrum. See Clark (1999) and references therein for a recent review of reflectance spectroscopy and the spectral features of geologic materials.

Reflectance of a particulate surface is complex and the optical path of photons is a random walk (e.g. see Clark and Roush, 1984). At each grain the photons encounter, a certain percentage are absorbed. If the grain is bright, like a quartz grain at visible wavelengths, most photons are scattered and the random walk process can go on for hundreds of encounters. If the grains are dark, like magnetite or charcoal, the majority of photons will be absorbed at each encounter and essentially all photons will be absorbed in only a few encounters. This darkens the reflectance in greater proportion than the number of dark grains in the sample (Figure 3a; see Clark, 1999 and references therein for reviews). The random walk process, scattering and the mean depth of photon penetration are discussed in Clark and Roush (1984).

The random walk process of photons scattering in a particulate surface also enhances weak features not normally seen in transmittance, further increasing reflectance spectroscopy's sensitivity as a diagnostic tool. Consider two absorption bands of different strengths, such as a fundamental and an overtone (see Clark, 1999 for definitions of fundamental and overtone). The stronger absorption will penetrate less into the surface, encountering fewer grains because the photons are absorbed. At the wavelengths of the weaker absorption, fewer photons are absorbed with each grain they encounter, so the random walk process goes further, increasing the average photon path length. The greater path length will result in more absorption, thus strengthening the weak absorption in a reflectance spectrum (Clark and Roush, 1984).

This random walk scattering process, while enhancing detection of some features, has a complicating side effect. The controlling factor in the scattering/absorption process observed in reflectance spectra is the cross-sectional surface area, which is approximately proportional to the product of grain size and abundance. Thus, the observed reflectance of a multicomponent particulate surface is dependent on the absorption strength as a function of wavelength and of grain sizes of each component

comprising the surface. The process is well understood from a theoretical basis (Hapke, 1981, 1993; Clark and Roush, 1984), and through observation (e.g. Figure 3b; Clark, 1999 and references therein).

The scattering process makes determination of abundances from reflectance spectra impossible unless the grain sizes and absorption coefficients of each component in a mixture are known (Clark and Roush, 1984). Absorption coefficients have been can be derived for pure materials. Grain sizes can often be constrained by measuring absorption bands of different strengths in observed spectrum, or derived from microscope images of the sample. However, without these independent measurements of grain size of each component and their optical constants as a function of wavelength, the abundance of any component can't be accurately constrained.
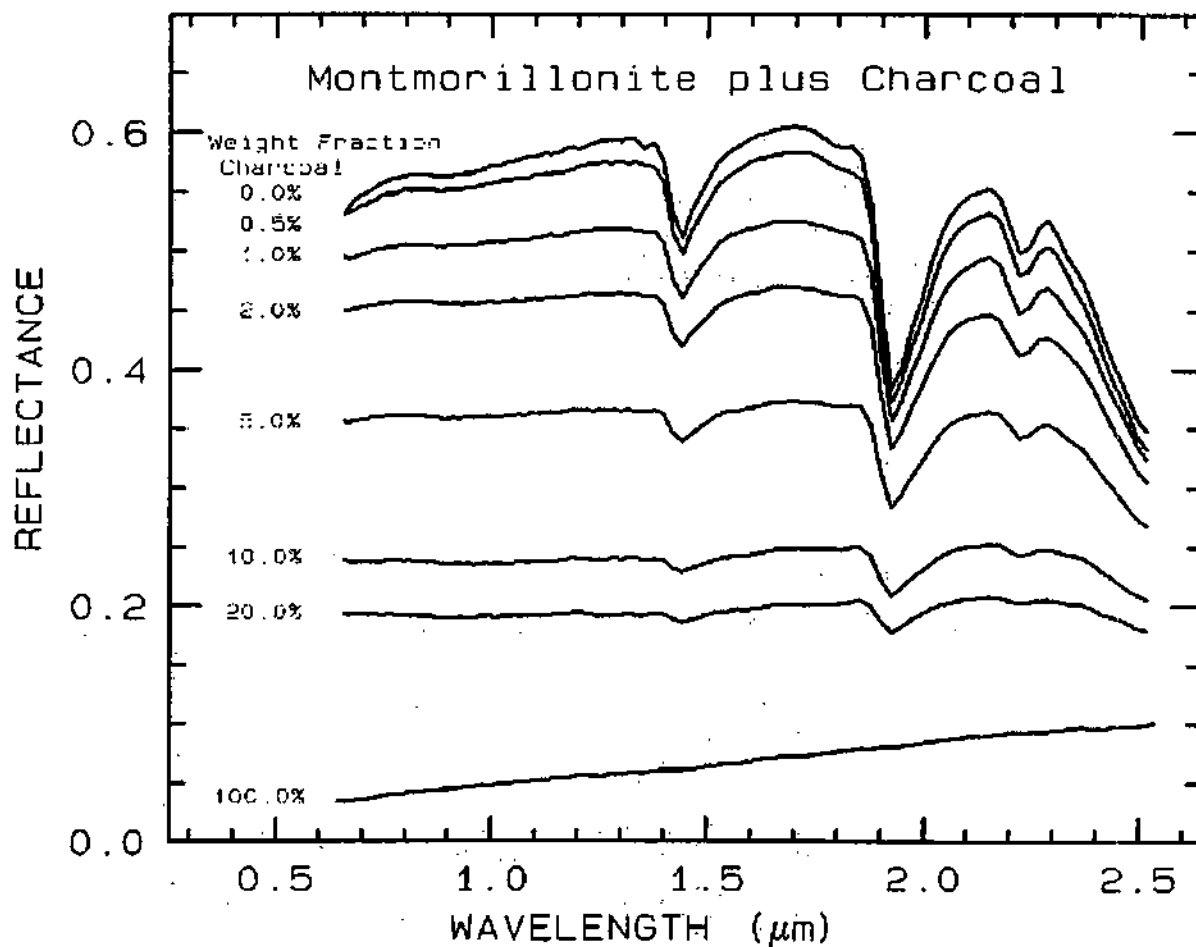
A rapid assessment tool need only detect the presence of the material of interest. However, understanding detection limits, which implies an understanding of abundances, is necessary for the success of such a tool. We show in this paper how reflectance spectroscopy can be used as a rapid assessment tool, even with the caveats on deriving abundances. Identification of detection failure modes is important so a sample can be sent for other testing and no sample slips through the test procedure as a false negative.

The objectives of reflectance spectroscopy as a rapid assessment tool is to screen many samples quickly, identifying those that do not need further assessment. The spectroscopy assessment may show such a strong amphibole signature as to not warrant additional testing, or have a certainty of non-detect to declare a sample "clean" of amphibole. An assessment tool should not have false negatives, meaning not detecting amphibole presence when it is truly present. It is acceptable for the method to not detect the amphibole when it is present as long as conditions can be identified to flag such a "not detectable" condition that would indicate another test is necessary. Spectroscopy can satisfy these conditions.

Spectroscopy of the electromagnetic spectrum could cover any wavelength region from gamma-rays to radio waves. For this study, we used visible to near-infrared (0.3 to 2.5 microns). This spectral range is the "reflected solar" range of the electromagnetic spectrum and commercial instrumentation is readily available with the specifications needed to resolve diagnostic absorptions to identify Libby amphiboles and other components in rocks and soils from the Libby region.

Reflectance spectroscopy may be sensitive to fibrous versus non-fibrous amphiboles. In a non-fibrous mineral, photons will tend to traverse in multiple directions through the crystal. But with fibrous minerals, it is a very low probability that a photon will traverse the long axis of a fiber, thus the absorptions along one crystallographic axis are not probed. Depending on the contribution to absorptions in the mineral's spectrum along that axis, a spectral feature may appear narrower or absent in spectra of fibrous minerals. This concept, reported here for the first time to our knowledge, will be examined at the end of this paper. We present evidence of a small narrowing of absorptions in spectra of fibrous Libby amphiboles compared to non fibrous minerals of similar compositions. This narrowing is not well resolved with current field portable instruments but is with Fourier Transform laboratory spectrometers, Thus, at present, the use of reflectance spectroscopy screening tool is for detecting the presence of amphibole mineralogy, and not whether it is fibrous or asbestiform.

Montmorillonite plus Charcoal

Weight Fraction
Charcoal
0.0%
0.5%
1.0%
2.0%
5.0%
10.0%
20.0%
100.0%

REFLECTANCE

WAVELENGTH (μm)

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Figure 3a, Montmorillonite-Charcoal mixture series illustrates the non-linear spectral properties of mixtures. Only a small amount of a dark material mixed with another material will dominate the spectral properties in greater proportion than the relative abundances. From Clark (1983).
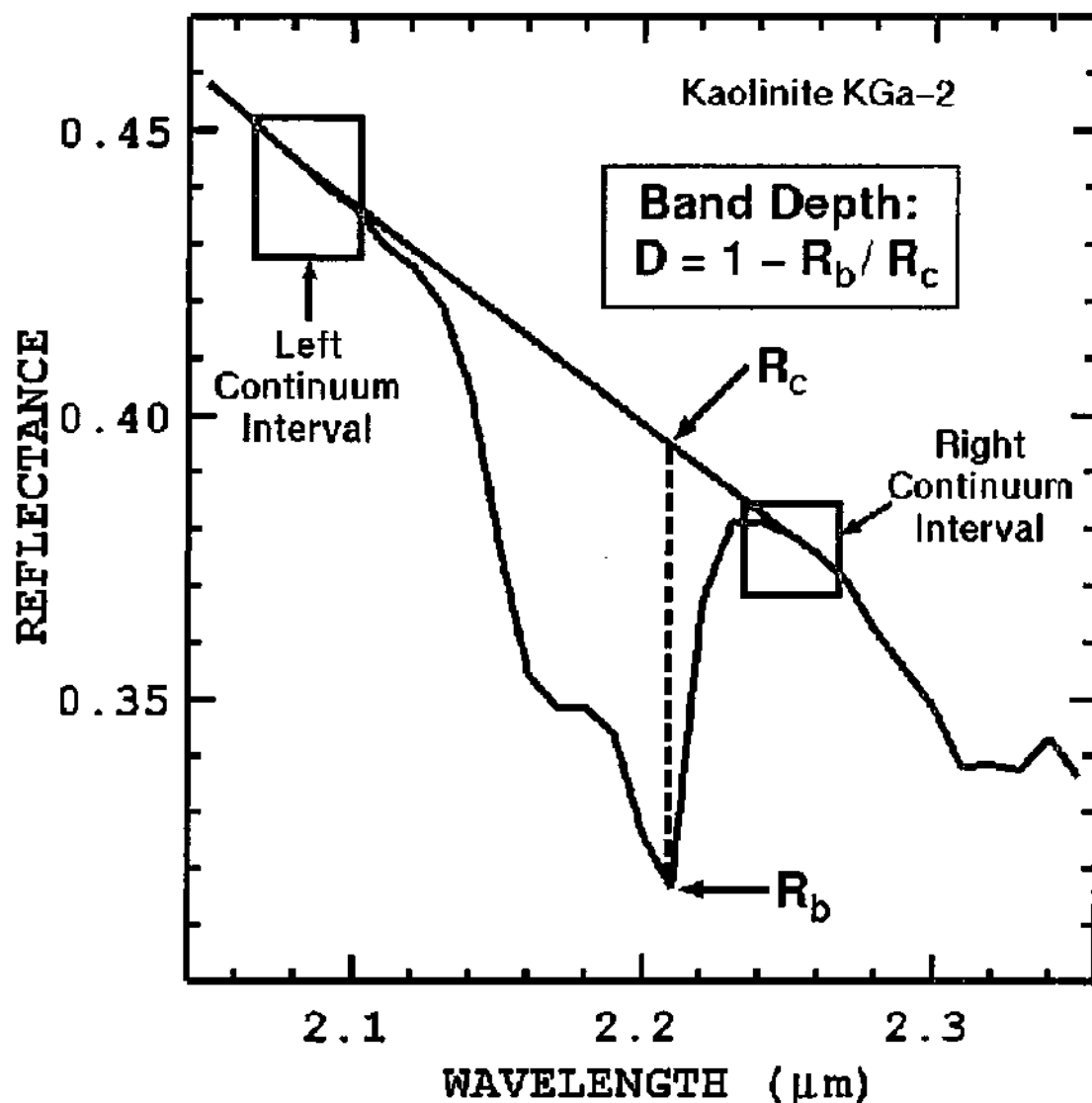
Charcoal grain
size range (μm)

Montmorillonite plus 10 wt%Charcoal
(< 63 μm)   various grain sizes
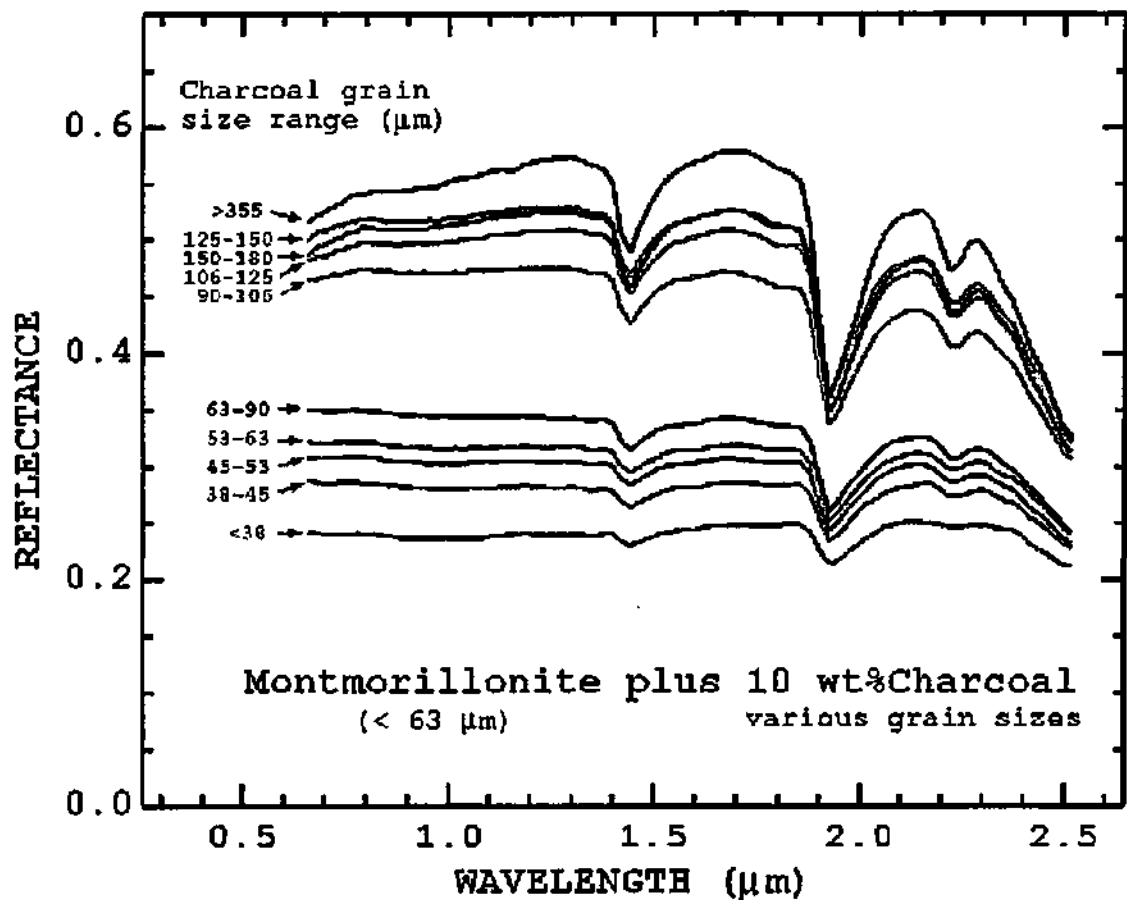
Larger 133 KB image

Figure 3b, Montmorillonite-Charcoal mixture series illustrates the non-linear spectral properties of mixtures. In this example abundance is constant and the grain size of the charcoal changes in each sample is verified. The cross-sectional area of minerals as seen by photons is the controlling factor, not simply abundance or grain size alone. From Clark (1983).

In the montmorillonite-charcoal reflectance curves in Figures 3a, 3b, the reflectance level changes as does the strength of the absorption features as a function of both abundance and grain size. The absorption feature strength, called the band depth, is defined relative to the continuum as shown in Figure 4. The band depth, D, is defined as

$$D = 1 - R_b/R_c,$$

where R_b is the reflectance at the absorption band center, and R_c is the reflectance of the continuum at the same wavelength as the band center (Clark and Roush, 1984). The continuum is an estimate of the absorption due to the spectral properties of other components in the sample, and may have curvature.

Figure 4. Band depth definition (Clark and Roush, 1984; Clark *et al.*, 2003).

An example of continuum definition and the detection of asbestos in a sample is given in the Clark *et al.* (2001) study of dusts from the World Trade Center. Chrysotile asbestos was found in small concentrations in many samples. The Chrysotile absorption feature, near 1.383 microns occurs on the wing of much stronger gypsum, muscovite and/or portlandite absorptions at longer wavelengths (Figure 5a; Clark *et al.*, 2001).

The continua for isolating the chrysotile absorption in the World Trade Center dust on Figure 5a must be curved for the most accurate definition. If a straight line continuum is used, only higher amounts of chrysotile would be detected, with approximately 1% limits, compared to about 0.25 % limit with the use of curved continua (Figure 5a, 5b; Clark *et al.*, 2001).
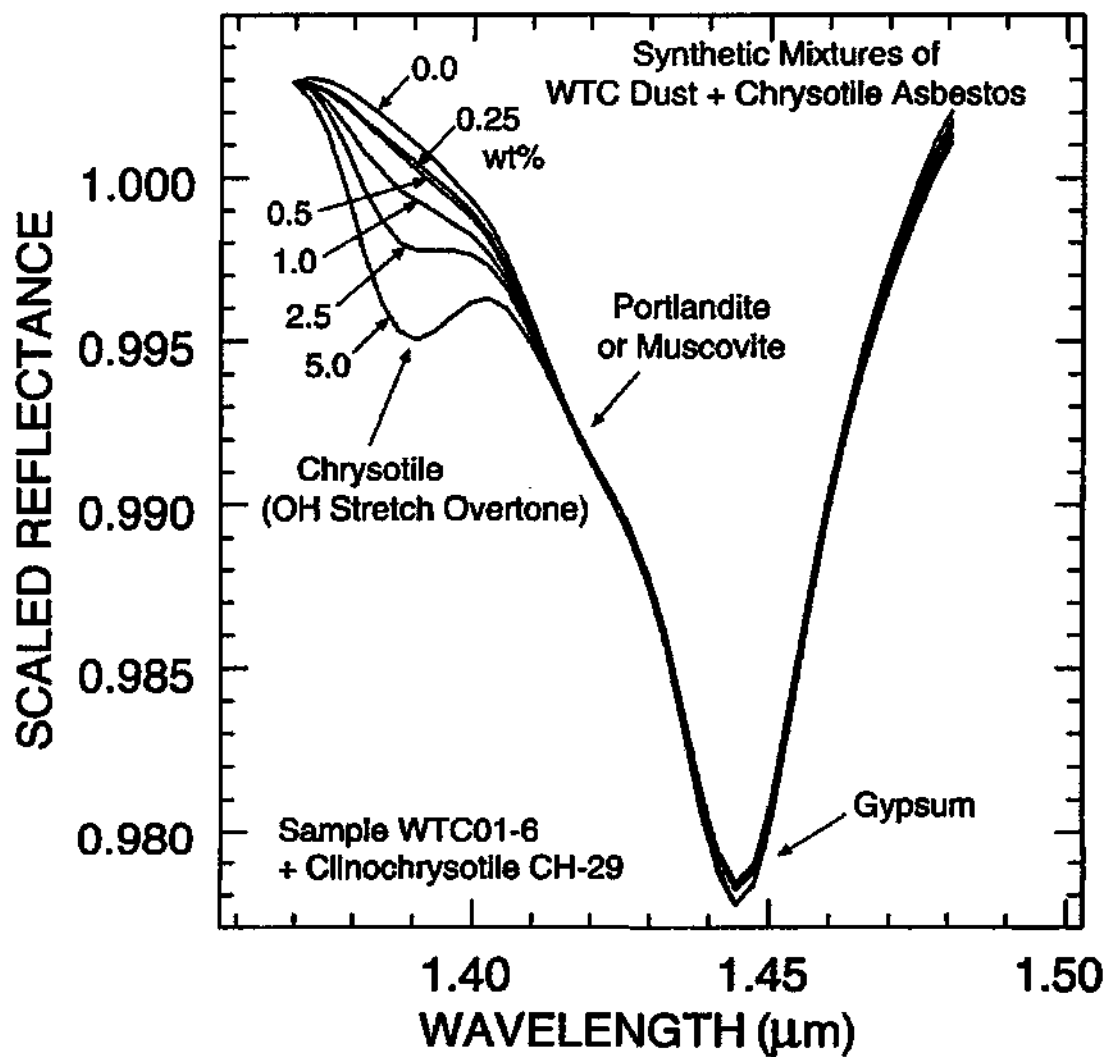
Larger 31 KB image

Figure 5a. Spectra of constructed mixtures of chrysotile and World Trade Center dust.
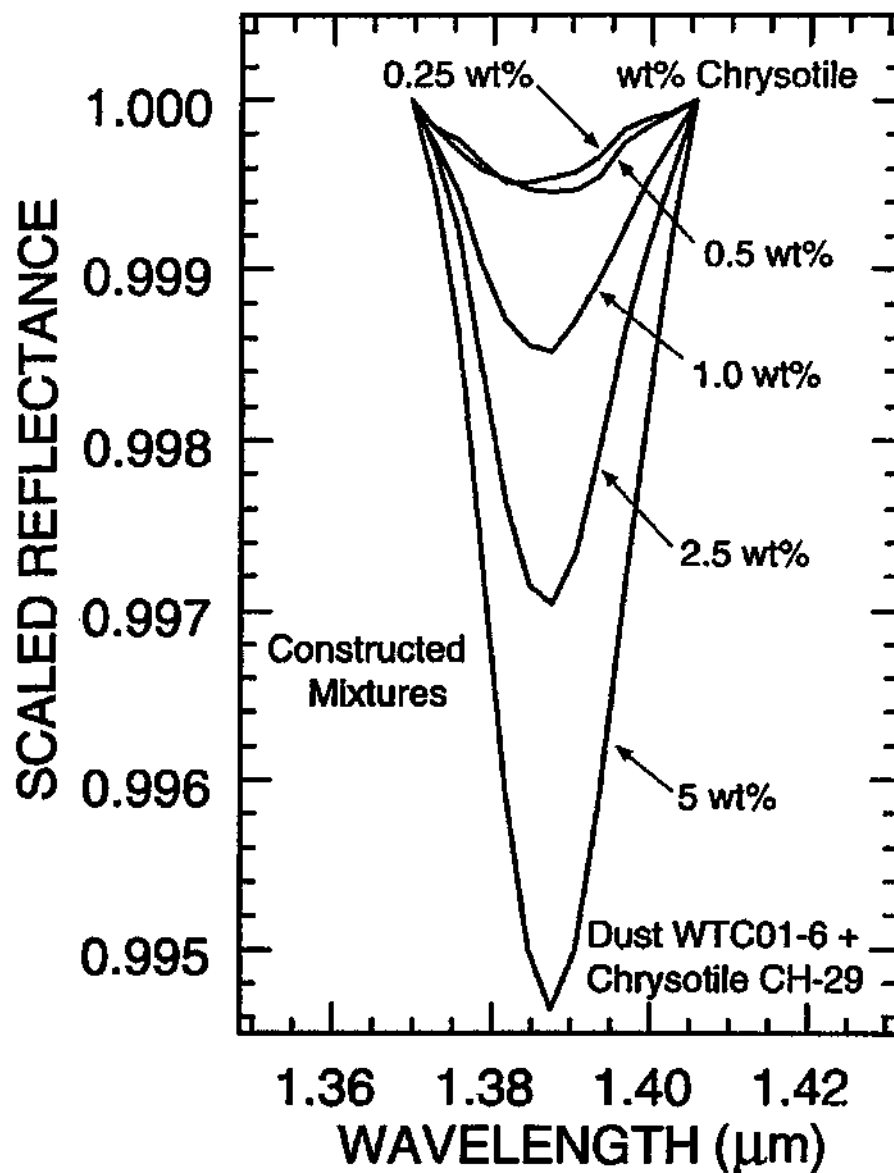
Larger 41 KB image

Figure 5b. Band depths of constructed mixtures of chrysotile and World Trade Center dust.

## Properties of Libby Vermiculite and Amphiboles

We have measured the reflectance spectra of thousands of EPA samples of rocks, soils, and other materials from the Libby, Montana region. Several dozens of these samples have also been analyzed by X-Ray Diffraction (XRD), Scanning electron microscopy (SEM) with energy dispersive spectroscopy for elemental compositions, and Electron Microprobe for elemental compositions. From these analyses, we find the "Vermiculite" ore contains at least 3 sheet-silicate phases: vermiculite, hydrobiotite (mixed layer vermiculite-biotite), and biotite. Hereafter, we refer the above 3 minerals simply as "vermiculite."

Wylie and Verkouteren (2000) have studied two amphibole samples from the vermiculite mine near Libby. They determined the amphibole in both samples to be winchite, partially based on the classification system of Leake *et al.*. (1997). Previously, the amphibole from the Libby site has been called soda tremolite (Pardee and Larsen, 1929; Larsen, 1941), soda-rich tremolite (Boettcher 1966b), and richterite (Deer *et al.*. 1963). Electron microprobe analyses of 30 samples shows the Libby amphiboles have a range of compositions spanning 6 different mineral names (Figure 6; from Meeker *et al.* 2002). While the spread of compositions cover 6 amphiboles, each individual sample from the 30 collection locations show smaller compositional range. The average of the 30 (Figure 6) falls into the winchite category, but individual samples we used in testing straddle the richterite-winchite border. For simplicity, hereafter, we refer to the compositions we used in testing as "richterite," or "Libby amphibole."
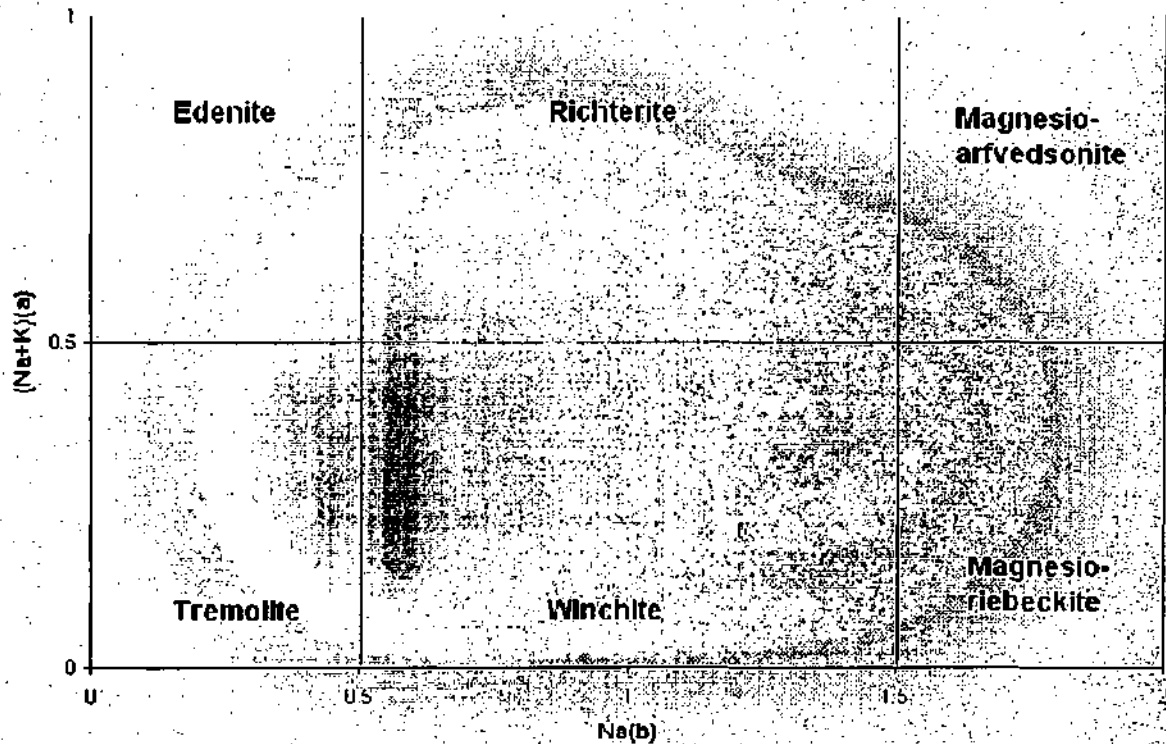
Larger 95 KB image

Figure 6: Generalized Libby amphibole compositions (from Meeker et al., 2003).

The Libby minerals display different levels of electrostatic charge. Each vermiculite, hydrobiotite, or biotite flake has shown some electrostatic charge, some more than others. Biotite flakes show the least charge, vermiculite the most. Ultrasonically washed "vermiculite" flakes still show charge. Richterite grains show significant charge. Richterite has been observed to electrostatically cling to vermiculite flakes.

Richterite grains have been observed to electrostatically jump to and/or cling to (Figure 7a, 7b, 7c) rubber, glass, porcelain, aluminum, and Libby vermiculite ore. The closest analogy to the observed properties is "the richterite grains appear like iron filings with everything being a magnet." These extreme electrostatic properties imply unusual mixing properties, make standards difficult to prepare because of possible clumping (Figure 8a, 8b) in natural as well as prepared samples and may result in heterogeneity on a small scale.

Detection of Libby amphibole contamination can be difficult in certain situations. Libby amphibole fibers sometimes grow in between vermiculite layers (Figure 1 and below). The index of refraction of vermiculite and the tremolite-richterite-winchite fiber compositions are nearly identical (vermiculite = 1.55-1.58, biotite = 1.61-1.70, tremolite = 1.61, Actinolite = 1.64: Hurlbut and Klein, 1993). Thus, normal optical microscopy methods may have difficulty distinguishing the presence of the Libby amphiboles intergrown with vermiculite and perhaps biotite (biotites tend to be very dark at optical wavelengths, adding additional difficulty). Surface methods such as TEM and SEM do not probe inside the vermiculite grains. In other cases, the fibers may be too small to easily detect with standard optical microscopy methods like PLM.

Figure 7a: Amphibole grains from the Libby, MT area show electrostatic charge. Here grains electrostatically cling to a ceramic pestle and are attracted to a rubber glove.

Figure 7b: Amphibole grains cling to the ceramic mortar as they are poured from the container.

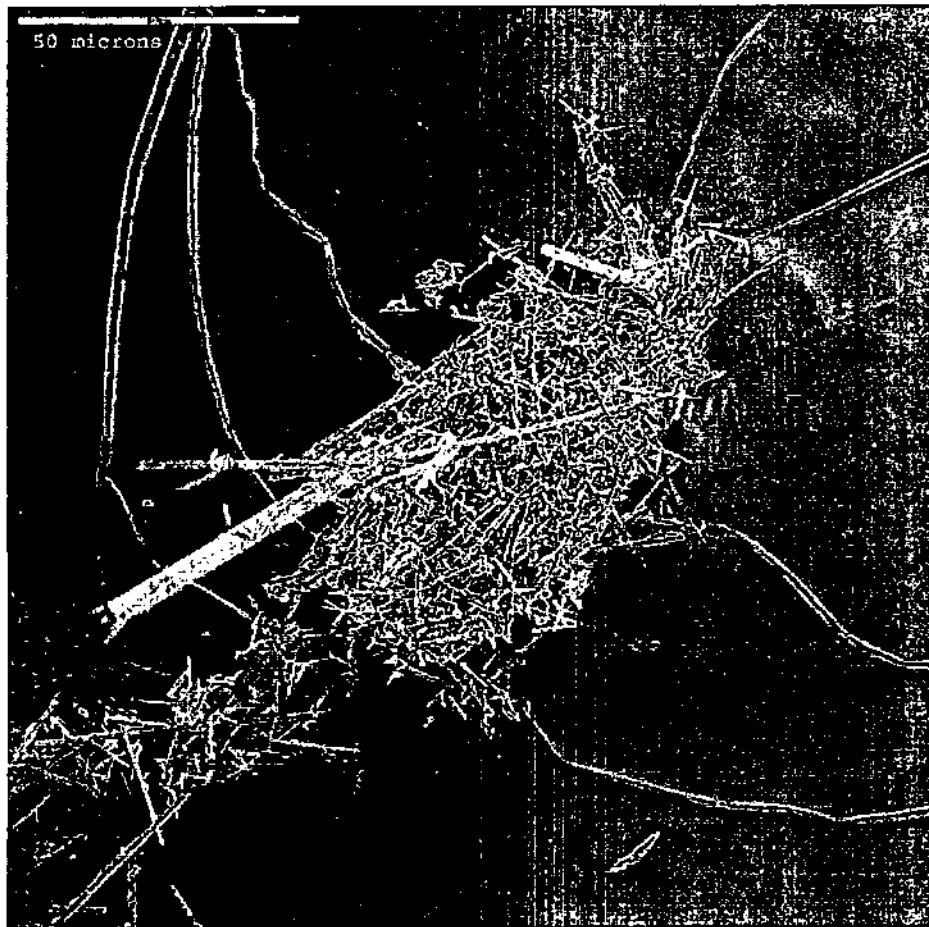Figure 7c: Amphibole grains from the Libby, MT jump from the ceramic pestle to a rubber glove due to electrostatic charge.
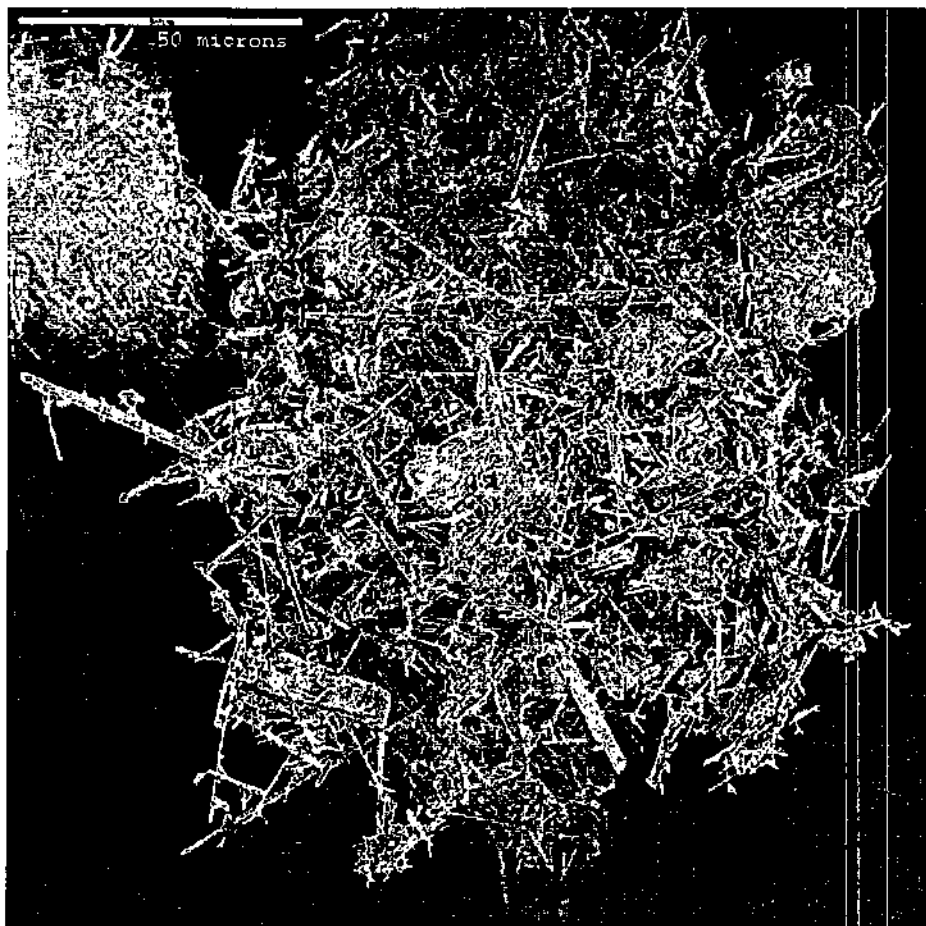
50 microns

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Figure 8a. A cluster of amphibole fibers. Such bundles are held together by static electricity.

Figure 8b. Another cluster of amphibole fibers. Such bundles are held together by static electricity. Some of the "chunky" looking clumps are larger amphibole "cleavage fragments," but others are unresolved clouds of fibers held together with static electricity. The larger image (click on the image link above) begins to show the fibers in these clumps.

Standards for Testing Spectroscopy Methodology

The USGS has been funded by the EPA to develop a set of standards for testing methodologies to detect Libby amphiboles. The details of the development of these test samples is beyond the scope of this document and will be reported elsewhere (S. Wilson, in preparation). Briefly, selected materials have been collected, ground and/or sieved to various grain sizes, appropriate fractions weighed, and physical mixtures created with soils and powdered minerals.

Among the concerns in standards preparation is uniformity on some reasonable scale so that methods can obtain close to the same answer within some error limit if that method were valid. For example, if testing needs 1% accuracy, the standard should be uniform on the scale of the sample measurement to at least 1%. The electrostatic properties noted above poses challenges in preparation of uniform standards. As a result, we have constructed numerous test standards to find a good procedure that can be used on a large scale. We produced standards with small-scale heterogeneity as well as small-scale homogeneity. Thus, the standards provide a possible cross section of different mixtures and uniformity that might be encountered in natural samples from the Libby region.

Of the methods being tested in this program, including PLM, SEM, TEM, XRD, and Reflectance Spectroscopy (RS), RS can rapidly probe the largest physical sample volume. Our near-infrared spectrometer can probe, for example, millimeters to many square meters in area. Photons penetrates tens of microns to several millimeters into a sample, depending on wavelength. This means that milligrams to kilograms of sample may be probed with RS. Thus, while uniformity may be an issue with some methods and some scales, RS can be used to probe the largest volume of material in a single measurement thus providing, in theory, a more uniform answer independent of small scale heterogeneities in the sample.

These standards, regardless of their uniformity, provide interesting tests of different matrices to which the amphibole is added and thus test a likely range of conditions that may be encountered in the real-world. We constructed mixtures using quartz, Libby soils, Denver Federal Center soils, and Libby vermiculite. Because Libby vermiculite may contain richterite fibers, we washed vermiculite flakes in an ultrasonic bath 19 times (14 times in water, 5 times in isopropyl alcohol. SEM images show some flakes still contain richterite (discussed below). Libby vermiculite includes some tremolite/winchite/richterite amphibole and the standards of vermiculite plus richterite therefore show more scatter in the lower concentrations. Amphibole used in the standards was obtained from fibrous amphibole veins at the Libby mine site. In general, standards were prepared for about 10% and less amphibole by weight. An exact listing of every standard will not be provided here as some standards are currently being used in blind tests at EPA and contractor laboratories.

We have studied the Libby materials and constructed standards with several methods, including:

- X-Ray Diffraction (XRD),
- Near-IR reflectance spectroscopy,
- Scanning Electron Microscopy (SEM),
- Energy Dispersive X-Ray Spectroscopy (EDS),
- Electron Microprobe (EPMA), and
- X-Ray Fluorescence (XRF).

Spectral Properties of Libby Materials

The visible to near-infrared spectrum of Libby vermiculite and Libby amphibole, hereafter referred to simply as richterite, is shown in Figure 9, at a spectral Full Width at Half Maximum (FWHM) of about 0.01 micron (10 nm). See Clark (1999) for a discussion of spectrometer resolution and FWHM. The richterite has diagnostic absorptions near 1.393, 2.31, and 2.36 microns. At higher spectral resolution, the richterite absorption appears sharper, which will improve detection ability in mixtures. Spectral resolution effects will be discussed in a later section.

The spectral properties shown in Figure 9 indicate some similarities between both vermiculite and richterite. Starting at short wavelengths in the ultraviolet, 0.35 micron, the reflectance of both minerals first rises to the green wavelengths near 0.5 micron. The UV absorption is due to ferrous iron in both structures. From 0.5 to beyond 1.2 microns is a broad absorption with small "ripples" on the curve, also due to ferrous iron (Fe^{2+}) in the structures. Initial measurements of vermiculites from other deposits also show iron absorptions but the strengths are different than those for the Libby vermiculites, thus the iron absorptions may be a fingerprint for Libby ore. A future paper will compare the spectra of different deposits and explore this possibility in detail.

Vermiculite contains both water and hydroxyl. The characteristic water signature is the H-O-H bend plus OH stretch combination band near 1.9 microns. The richterite spectrum (Figure 9) shows little absorption near 1.9 microns indicating only trace H_2O molecules are present. The small weak 1.9-micron features are likely due to water absorbed on the surfaces of the mineral grains.

More important absorptions in both vermiculite and richterite are the absorptions due to hydroxyl, OH, near 1.4 and 2.3 microns (Figure 9). The small shifts and shape differences are highly significant, and are typical of the differences between OH-bearing minerals (e.g. Clark et al. 1990). The 1.393-micron richterite absorption is shifted from the main OH/water vermiculite feature near 1.4 microns as well as from other OH-bearing minerals. No other mineral is known to have an absorption at this wavelength with this feature width. Therefore, it is a diagnostic absorption of the tremolite-winchite-richterite mineral (the chemistry influence the on OH absorption position is small in this series so the spectra appear similar). In fact, there is little change in the feature position from tremolite to actinolite at the spectral resolution of these data (higher spectral resolution my reveal more differences).
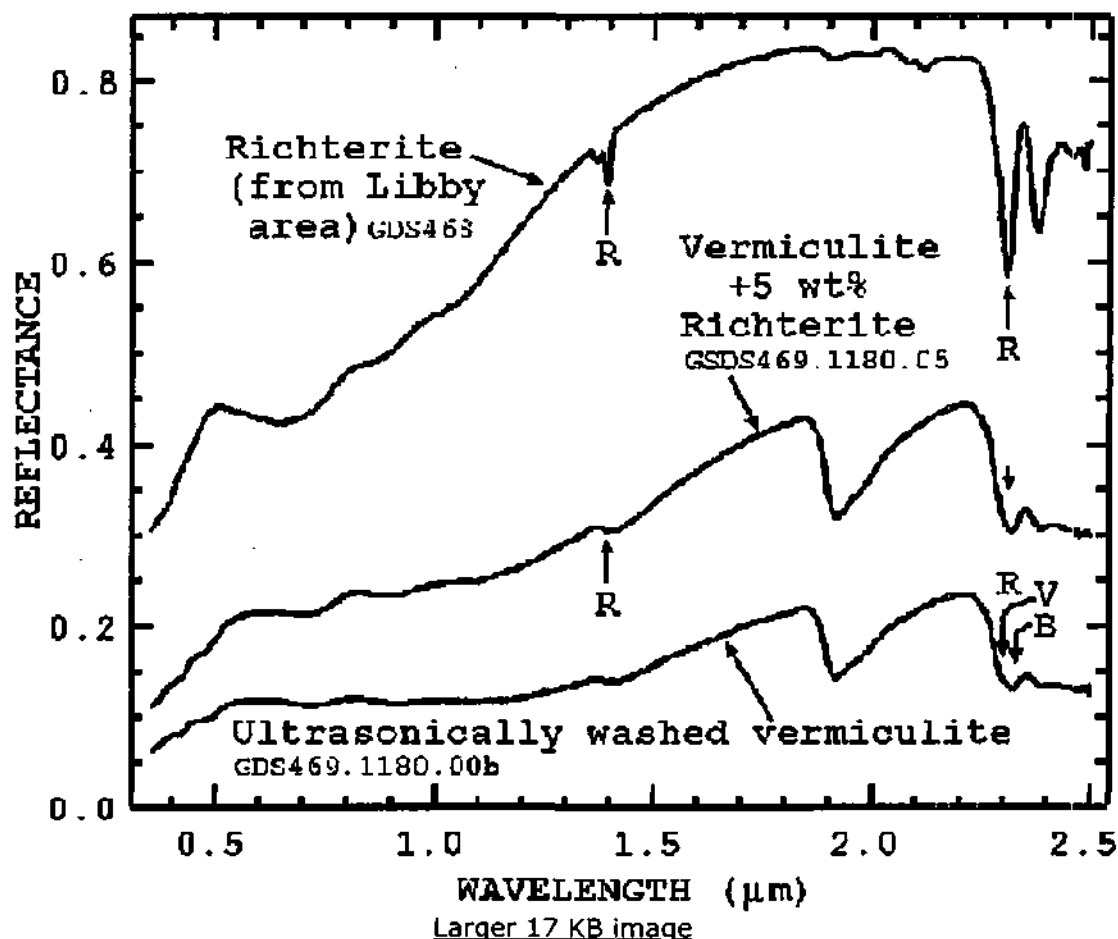
Figure 9. Measured spectra of real samples: Libby richterite (top), Libby vermiculite, washed 19 time in ultrasonic baths (bottom), and a constructed mixture of washed vermiculite and richterite (middle). The letter "R" points to richterite absorptions, "V" to vermiculite absorption, and "B" to biotite absorption.

The first standard prepared used ultrasonically washed vermiculite flakes, unpuffed, about a centimeter in size and a fraction of a millimeter thick. The vermiculite, shown in Figure 9, was mixed in different proportions with richterite and the spectra of each mixture was measured. An example mixture spectrum is shown in Figure 9, middle curve. On the scale of the plot, the richterite absorptions appear weak, but by continuum removal can be isolated and measured with high accuracy. A plot of the observed 1.393-micron richterite feature strength is shown in Figures 10a and 10b. At low values of added richterite, the observed data do not follow the expected trend (Figure 10b). X-ray Diffraction data of these samples also departs from the expected trend. The reason for this departure, as we have already indicated is due to richterite fibers inside the vermiculite flakes.
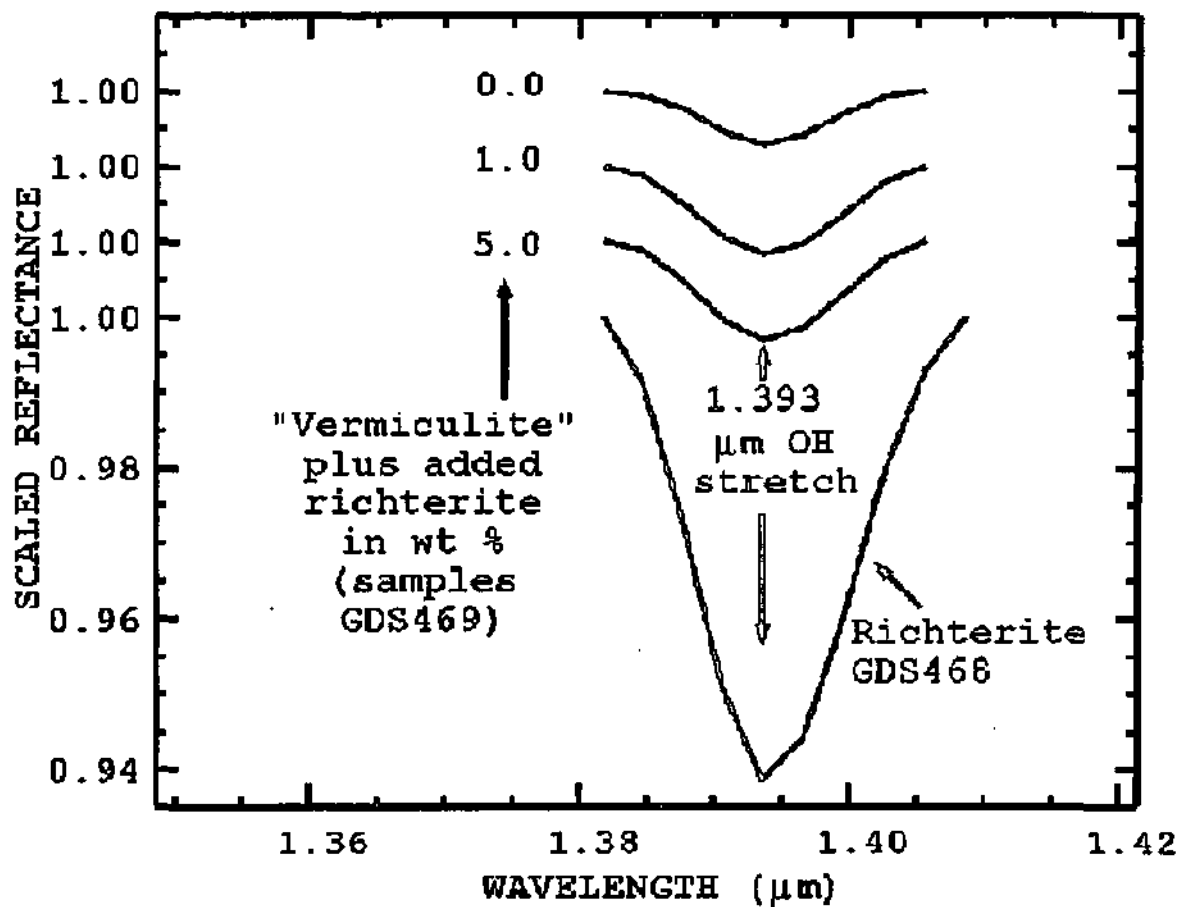
Figure 10a. Measured 1.393-micron richterite absorption strength is shown for constructed mixtures of richterite and the ultrasonically washed vermiculite. The ultrasonically washed vermiculite still shows a 1.393-micron feature. This feature indicates residual richterite in the vermiculite.

Ultrasonically washed
Libby Vermiculite plus
added Richterite

1.393 micron OH-stretch
feature strength

Added Weight % Richterite

Larger 13 KB image
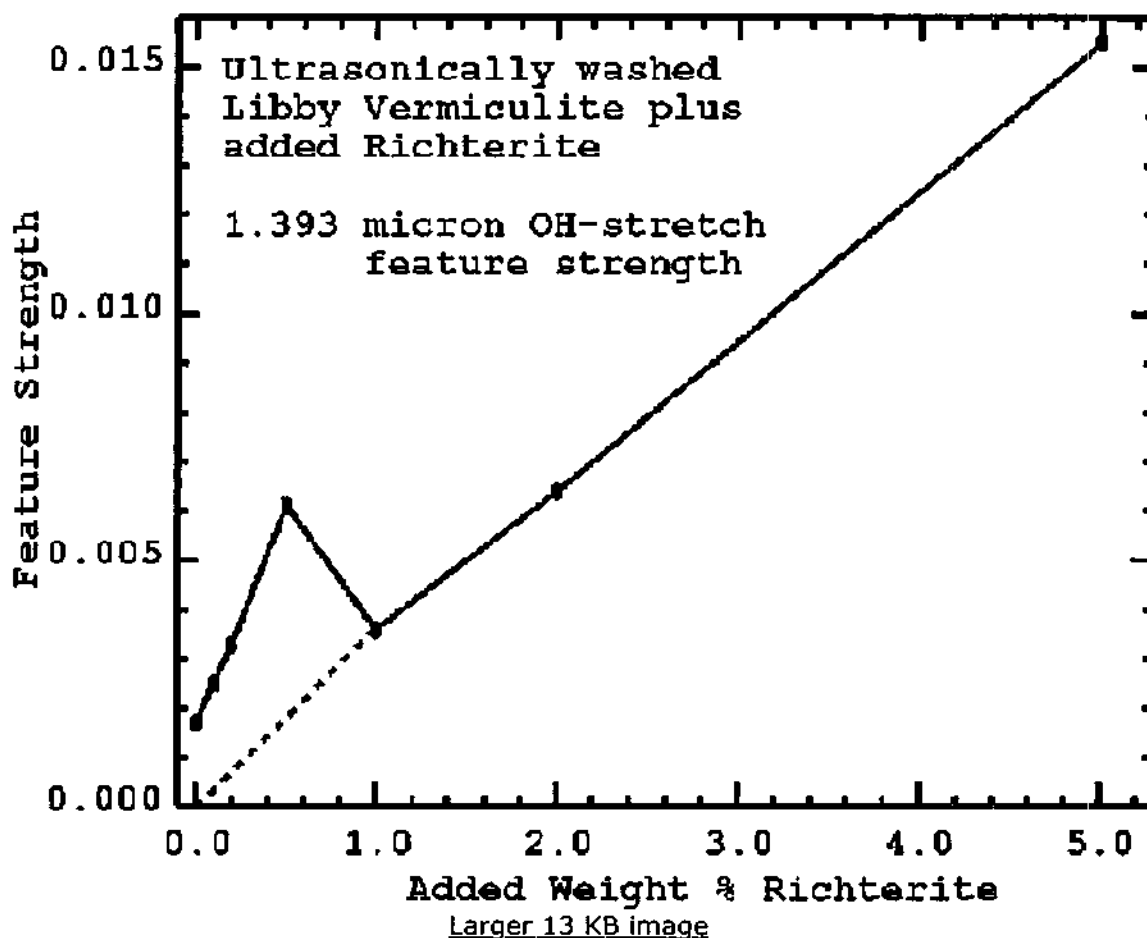
Figure 10b. The measured 1.393-micron feature strength from the combined mixtures. The error bar in determining the feature strength is approximately the size of the points. The deviation from the trend line (dashed line) is due to residual richterite in the ultrasonically washed vermiculite. Compare with the observed XRD results in Figure 11. For higher concentrations of richterite in the sample, the richterite coats the vermiculite grains and thus hides the residual richterite in/on the washed vermiculite flakes, so the variability is masked.

XRD plots of richterite added to vermiculite
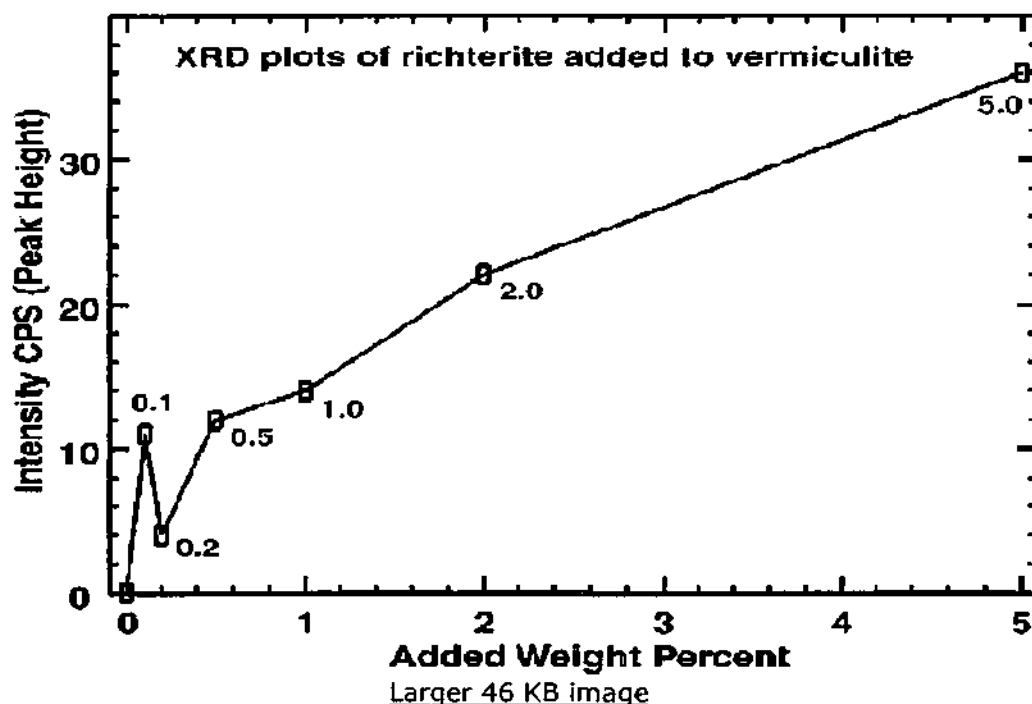
Figure 11. XRD peak height for constructed Libby vermiculite + richterite mixtures. The error bar in the measurement is approximately the size of the small rectangles. The large variation in the trend at low added weight percent richterite is due to the residual richterite in the vermiculite. Higher concentrations of richterite in the sample masks the variability in the cleaned vermiculite flakes. The reflection that was used for the peak height was the htl=(110) lattice plane, with d-spacing of about 8.45-8.56 angstroms.

In an effort to determine the extent of richterite inside vermiculite vermiculite flakes, a number of individual, ultrasonically cleaned flakes were measured with reflectance spectroscopy. The observed 1.393-micron richterite absorption was found to be quite variable in strength (Figure 12). Optically, we could detect no fibers inside the vermiculite, likely because of the close values of the index of refraction between the two minerals, as noted previously.

One vermiculite flake, flake 7, indicated the strongest 1.393-micron absorption strengths, with the implication of the most richterite in/on the flake. The flake was split with a razor blade in clean environment and pieces were examined with scanning electron microscopy (SEM). Images of one piece, 7A are shown in Figure 13a and 13b. While it is impossible to prove any one amphibole fiber in these images grew between the vermiculite layers, the correspondence here in these images with the higher amphibole abundance observed by spectroscopy and the undisputable fact of fibrous amphibole inside vermiculite flakes on a macroscopic scale from Figure 1 provides definitive evidence that the amphibole occurs inside vermiculite. Many such flakes have been observed, when split open in the field, to show the fibrous amphibole. So, while not every vermiculite flake contains the amphibole, many do.

This spectroscopic result, the individual flake results in Figure 12, the XRD results, and the observed electrostatic properties indicates the richterite abundance is highly variable and cannot easily be cleaned from the vermiculite. Randomly selected *small* samples could detect large or virtually no richterite (see flake variability in Figure 12). Even with sample a preparation process that includes liquids to clean a larger sample, richterite could still adhere to the vermiculite. Thus, detection in any environment can be inconsistent unless sampling can be done on a large sample volume, probing the sample undisturbed and unprocessed, such as can be done rapidly with reflectance spectroscopy. Yet to be understood is how/if the richterite fibers can be released to become airborne. What electrostatic/mechanical/humidity/other conditions will permit that release?

The importance of this discovery indicates that where unprocessed Libby vermiculite is present, even though no amphiboles are visible, there is a possibility of fibrous amphiboles occurring within the vermiculite. Disturbing the vermiculite, such as driving over flakes in a car, could break open flakes, possibly releasing fibers into the environment where they could become airborne and inhaled.

Larger 13 KB image
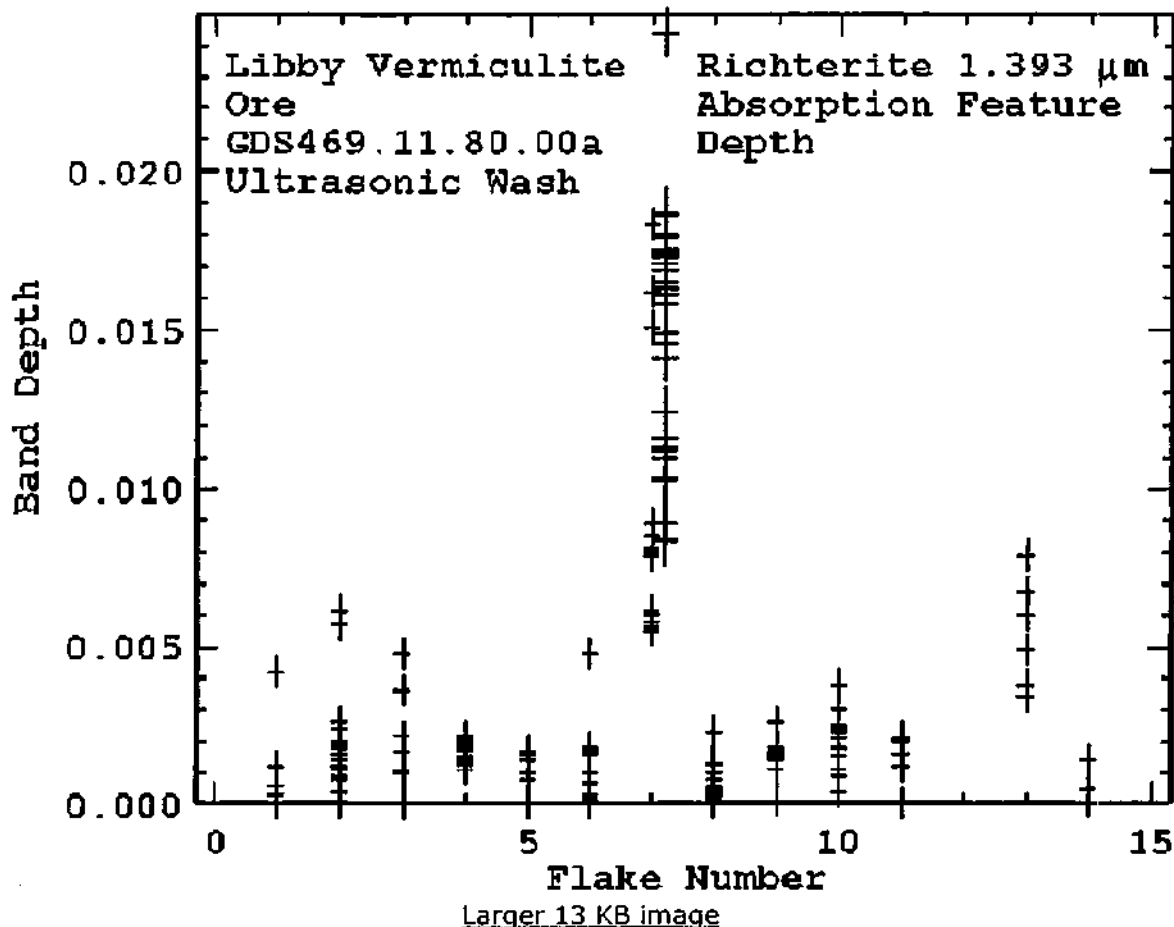
Figure 12. Measured spectra of individual Libby vermiculite flakes are shown for the 1.393-micron richterite absorption feature. The vermiculite was washed in ultrasonic baths 19 times, yet these measurements show certain grains still contain richterite. Flake 7 showed the highest spectral indication of richterite, so the flake was split with a new, cleaned razor blade and individual pieces measured. One of those pieces (the second set of measurements to the right of the "7" line on the plot) showed very high spectral indications of richterite. This piece showed many microscopic vein-like structures in the flake through a stereo microscope. SEM images of these flake are shown in figures 20-22, and show richterite fibers.
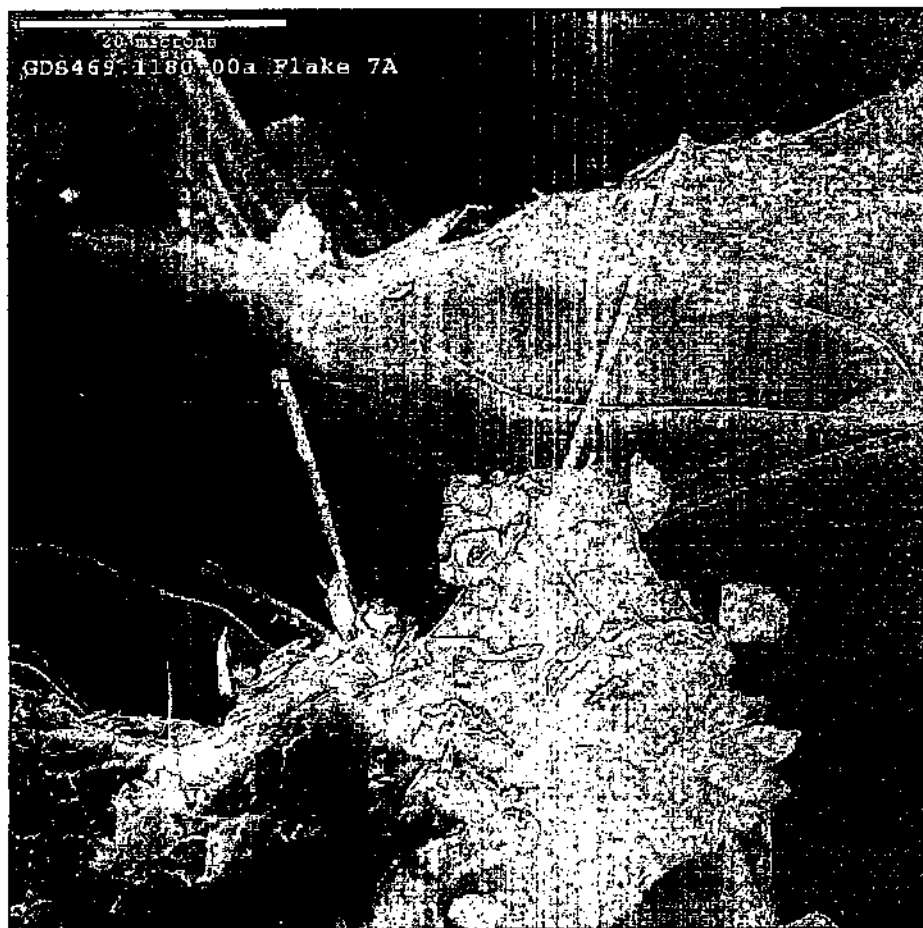
Larger 137 KB image

Figure 13a. SEM image of a split portion of flake 7 (see Figure 12), called flake 7a, shows richterite fibers sticking out of the edge of the flake. The richterite fibers are the long thin structures pointing from near center toward the top of the image. Are the fibers embedded in the vermiculite, or were they electrostatically adhering to the surface of the (19 times) ultrasonically washed flake and became embedded in the side during splitting of the flake?

Figure 13b Another image of flake 7a showing a richterite fiber (composition consistent with amphibole Na-tremolite/winchite/richterite by energy dispersive spectroscopy (EDS) on the SEM) in the side of the vermiculite fibers. Again, did this fiber get embedded in the side during sample handling or did the richterite grow embedded between the vermiculite layers?

Radiative Transfer Reflectance Spectroscopy Modeling:

In order to better understand the observed trends in the constructed standards, radiative transfer modeling was done. The methods used are those described in Hapke (1981, 1993) and Clark and Roush (1984). We computed data for two general models: particulate scattering and molecular mixtures. Particulate scattering simulates the physical mixture of two or more components, each with its own grain size and abundance. The model assumes the grains are randomly distributed, and photons scatter on a mineral-air boundary. The molecular mixture assumes no scattering between mineral types and is analogous for our case to richterite grains embedded in vermiculite flakes. The model currently does not include grain shape.

Example computed spectra are shown in Figure 14a with continuum-removed 1.393-micron absorption depths shown in Figure 14b. The trends in the 1.393-micron depth as a function of abundance are shown in Figure 15. The corresponding trends in the 2.31-micron absorption are shown in Figures 16a and 16b.

The radiative transfer modeling shows that the observed trends in absorption feature band depths as a function of mixture abundance is not a straight line, and that different mixtures will produce different trends.

Computed Vermiculite + Richterite Mixtures
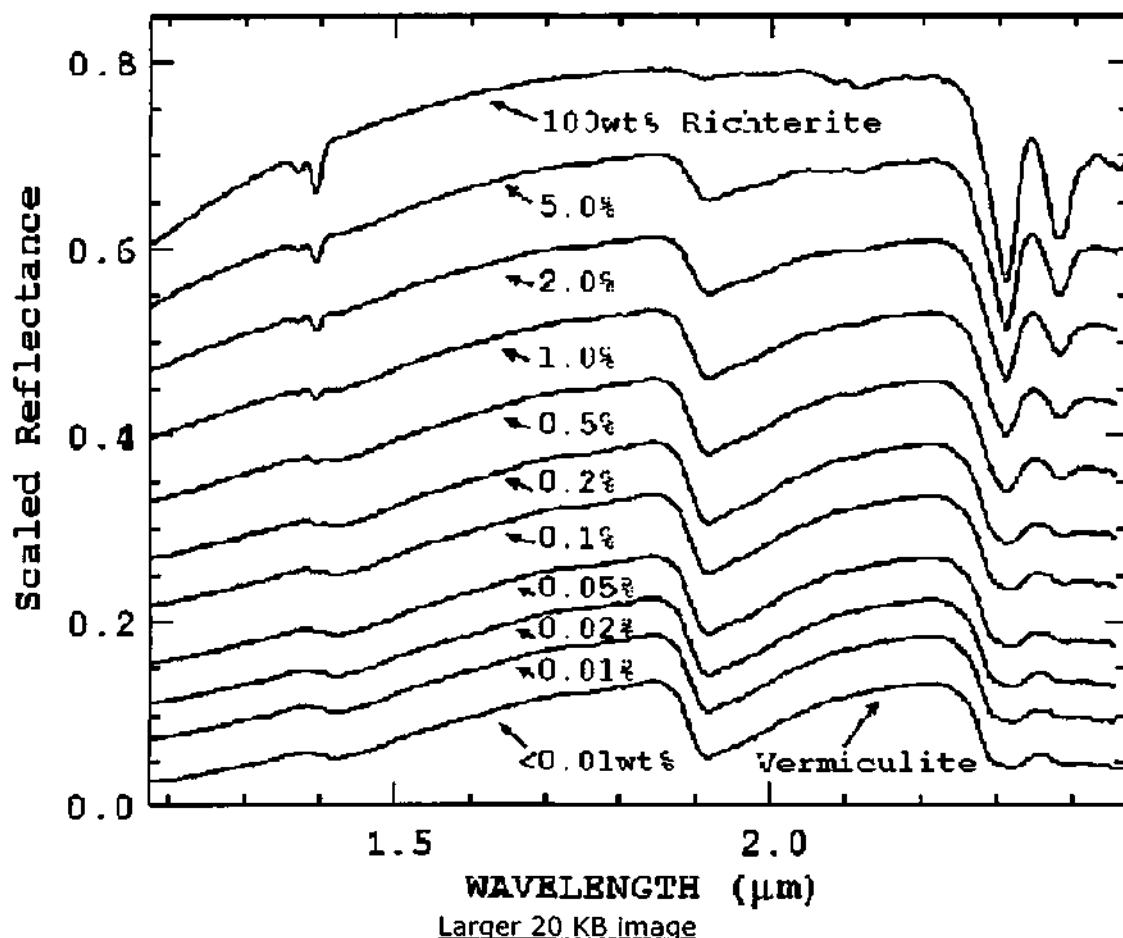
Figure 14a. From the derived optical properties of Libby vermiculite and richterite, a series of spectra were computed to illustrate the expected trends in spectra of richterite - vermiculite mixtures. A richterite grain diameter of 0.5 microns on centimeter-size vermiculite flakes was used for these calculations. Richterite shows strong absorption features at 1.393, 2.31 and 2.39 microns. The absorption feature strengths for other grain sizes would be different from those shown here.
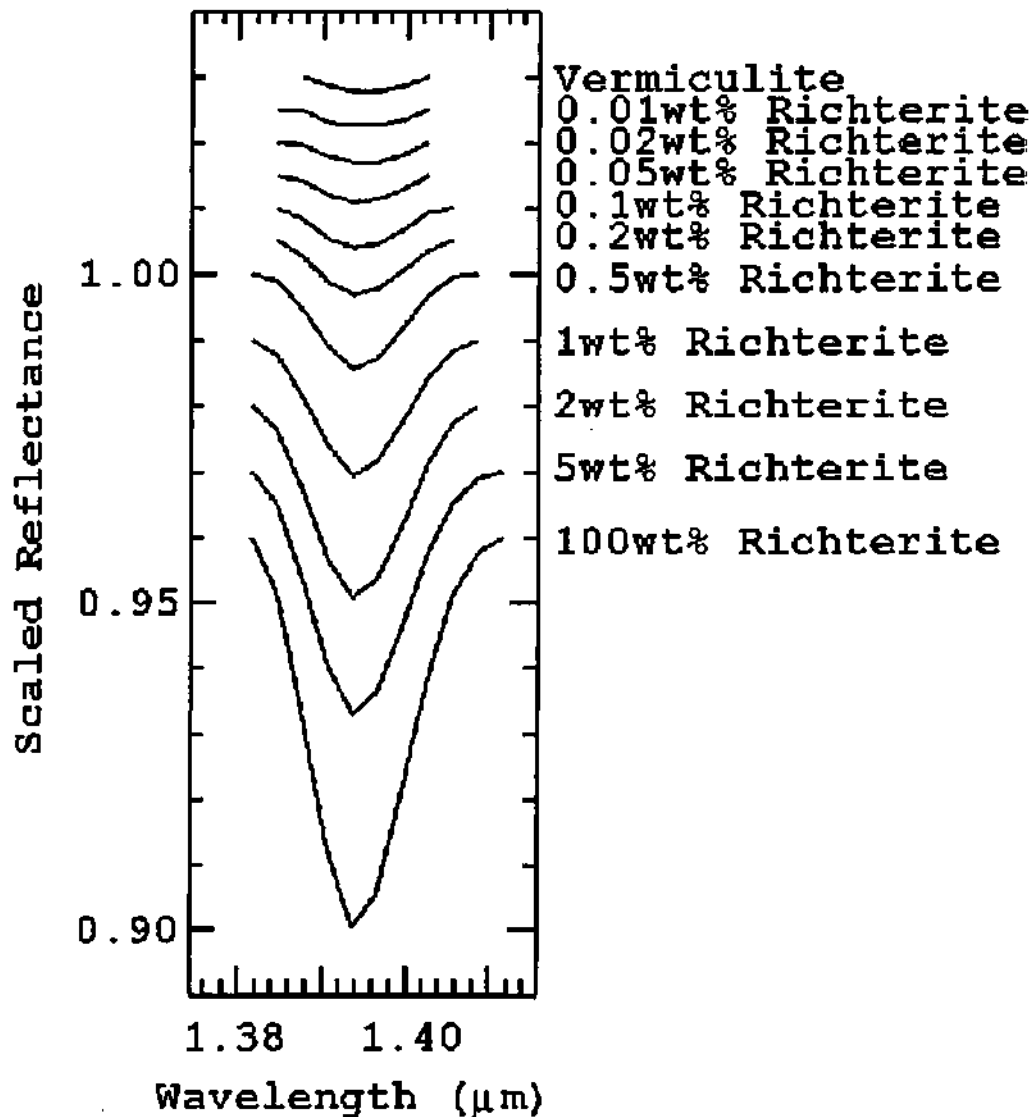
1.393 μm Feature

Figure 14b. The 1.393-micron richterite absorptions are shown from the modeled spectra in Figure 14a. The residual feature in the vermiculite spectrum (top spectrum) is probably indicative of trace richterite in the vermiculite sample from which the optical properties were derived, even after the vermiculite was ultrasonically washed 19 times.
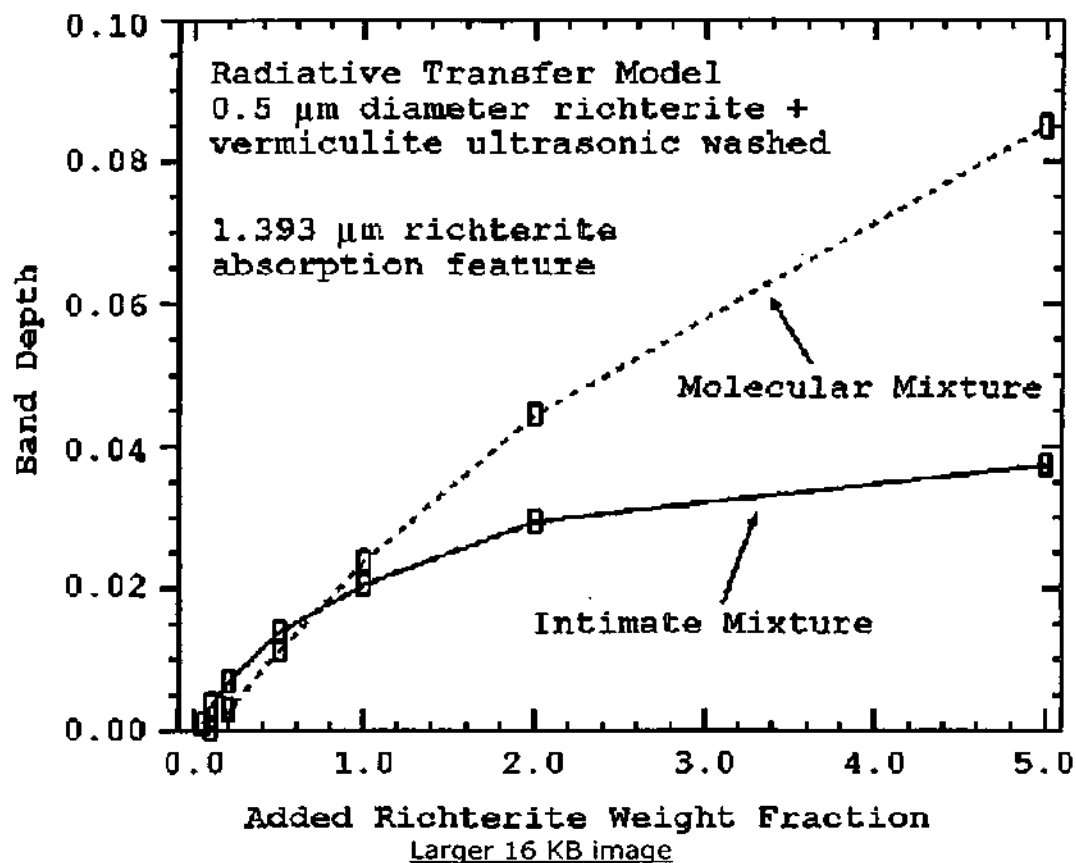
Figure 15. The 1.393-micron richterite feature strength model for intimate mixture (from Figure 14a) and for richterite embedded in the vermiculite flakes (molecular mixture model) is shown. Different grain-size distributions will change the magnitude of the feature strengths but the overall trends will be similar. The intimate model assumes a random mixture of grains of vermiculite, richterite.

2.31 µm Feature

Vermiculite
0.01wt% Richterite
0.02wt% Richterite
0.05wt% Richterite
0.1wt% Richterite
0.2wt% Richterite
0.5wt% Richterite
1wt% Richterite
2wt% Richterite
5wt% Richterite
100wt% Richterite

Scaled Reflectance

WAVELENGTH (µm)
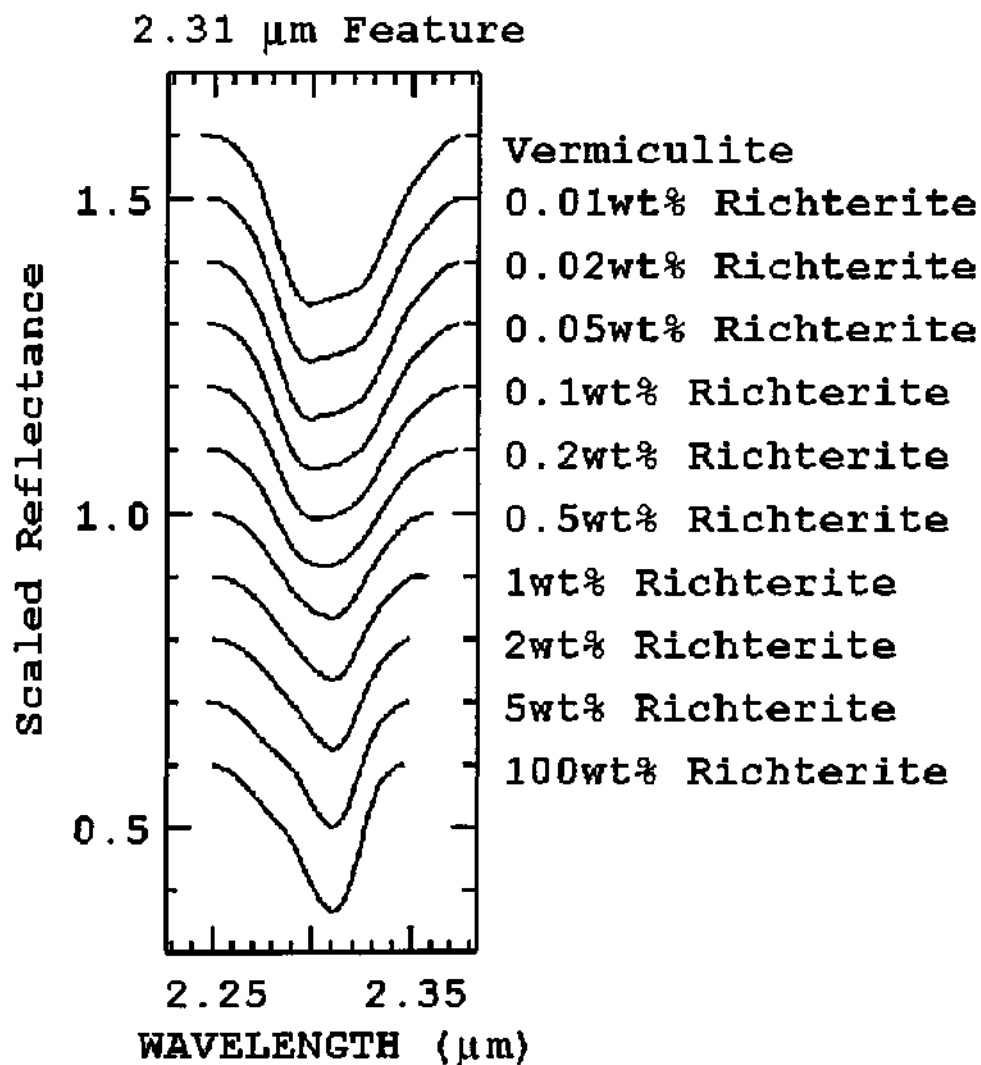
Figure 16a. The feature strengths for the 2.31-micron richterite absorption are shown from the modeled spectra in Figure 14a.
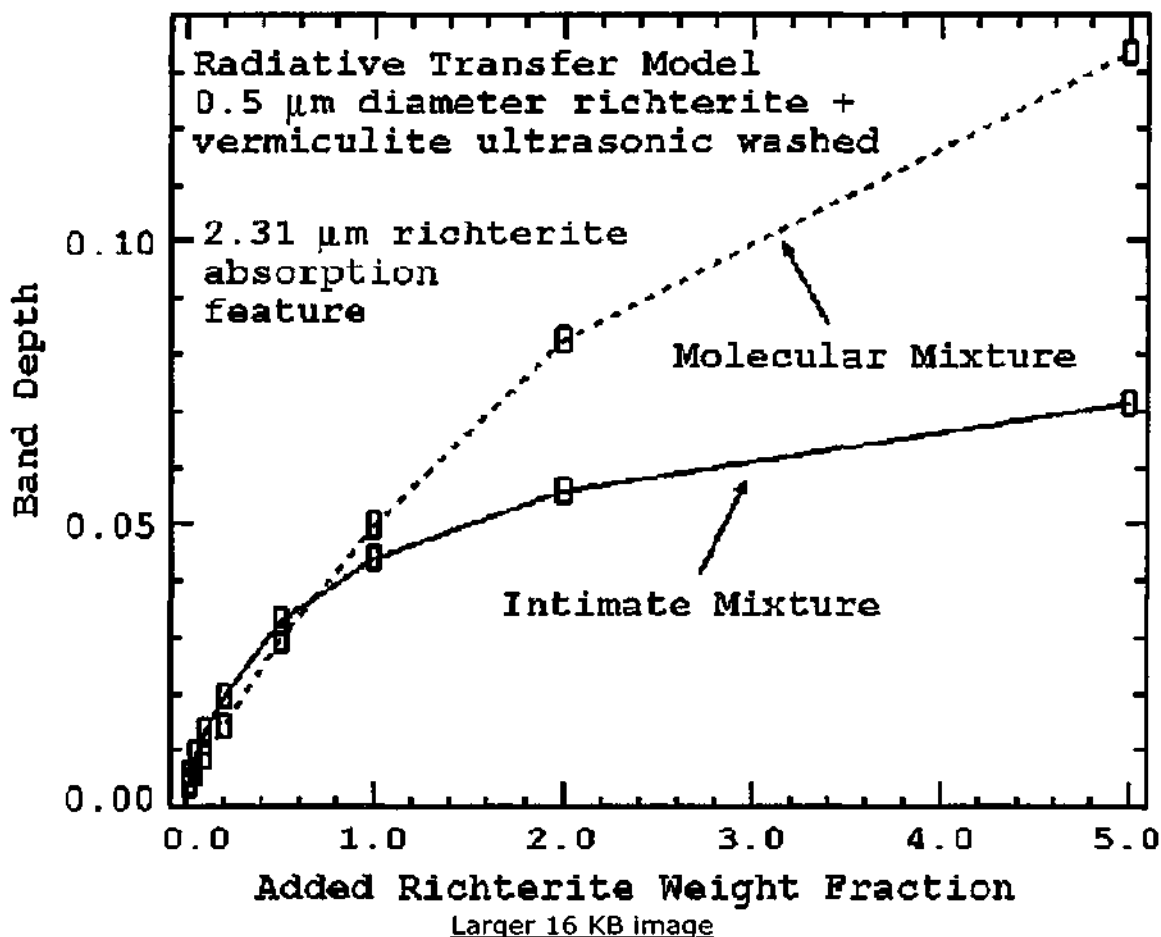
Figure 16b. The 2.31-micron richterite feature strength model for intimate mixture (from Figure 16a) and for richterite embedd
in the vermiculite flakes is shown. Different grain size distributions will change the magnitude of the feature strengths but the
overall trends will be similar.

In order to separate the spectral effects of the richterite absorption from the broader vermiculite absorption, a narrower continuum
was defined to produce the information in Figures 16a, 16b. The continuum definition is illustrated in Figure 17.
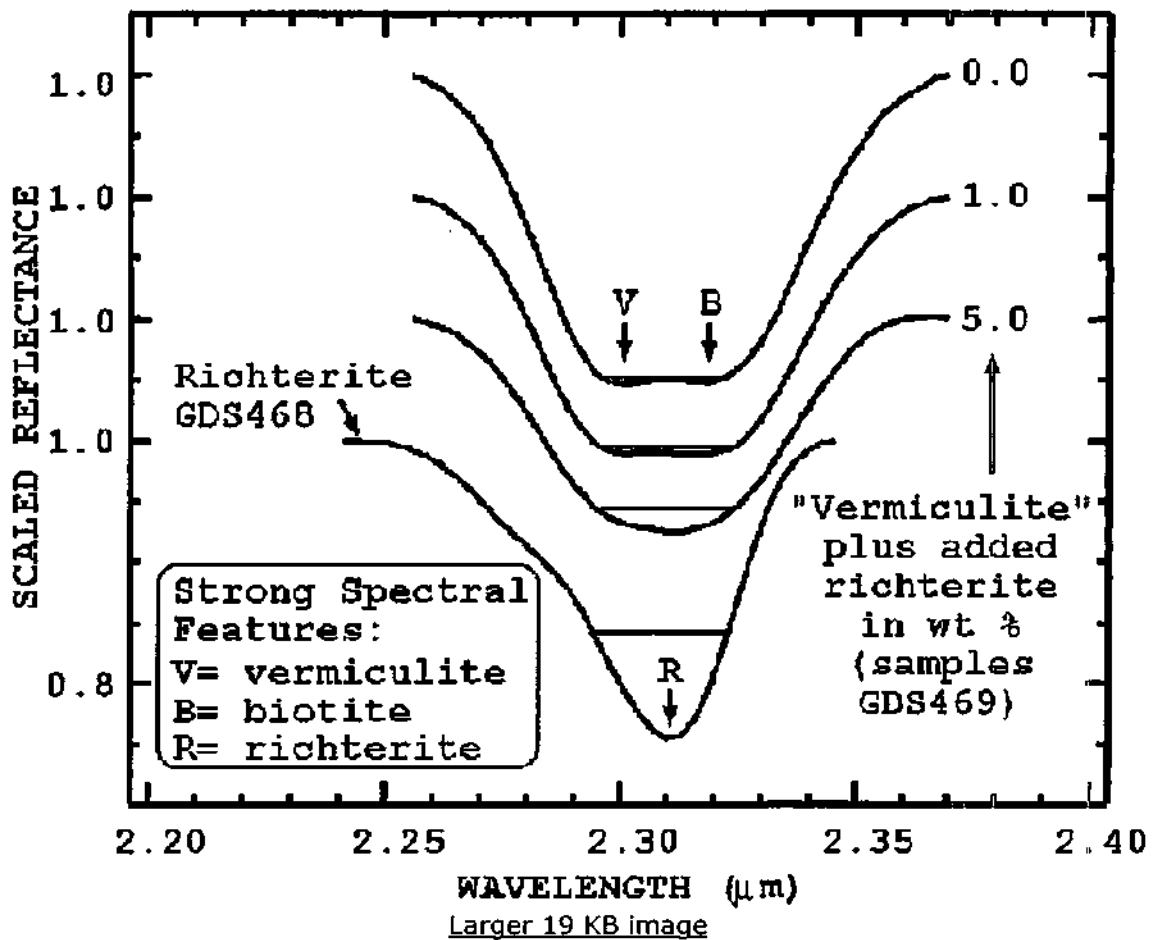
Figure 17. Same spectra as in figures 9 and 10a of constructed mixtures (not radiative transfer computed spectra), but showing the 2.31-micron feature. This feature is a combination of 3 sources: vermiculite (v), biotite (b), and richterite (r). The richterite indicator changes the curvature of the combined absorption feature. The red line indicates a continuum that is relatively insensitive to the vermiculite absorption but is sensitive to the center portion of the richterite absorption.

Spectroscopy Trends of Standards

As discussed previously, the trend in observed feature strength as a function of mixture abundance should not be straight lines, and depending on the reflectance of the different components and their grain sizes, we should observe different trend lines with different standard series. Indeed, this is the case, as shown in Figure 18.

The different trend lines in the standards all indicate richterite levels below 1% by weight can be routinely determined. Confusion increases when abundances fall below about 0.5 wt %. As the matrix material in the mixture becomes less absorbing, photons are able to travel further into the sample, potentially encountering more richterite grains. This is the case for the quartz series. Here, quartz absorbs little in the near infrared and the sensitivity for detection of richterite grains improves to at least 0.01 wt % (Figure 19). This indicates that if a sample is dark, for example it is wet (water strongly absorbs near-infrared photons), any sample processing that can raise the reflectance (without significantly decreasing grain size) will improve detectability. In the case of wet samples, drying them will improve detectability of Libby richterite.

Because spectroscopy shows absorptions of the matrix material (e.g. see Figures 5a, 9, and 14a) and the general reflectance level of the mixture, interferences can readily be identified. This allows the analyst to determine when conditions exist where reflectance spectroscopy would be limited and thus further testing is indicated. This fact makes reflectance spectroscopy a good rapid assessment tool that can still avoid false positives and negatives.

The variability in observed trends in spectral feature strength versus abundance shown in Figure 18 is indicative of sample inhomogeneity. All samples prepared thus far show this effect at some level. The ISTM-2 series, completed after gaining experience with preparation of other samples, still shows chunks (Figure 20a, b). However, these chunks are observed in real-

world samples from the Libby region so sample inhomogeneity mimics real-world experiences. The signal observed in any one measurement is then dependent on how many such clumps/chunks are near the surface. This presents a sampling challenge for all methods and will likely limit derived abundance accuracy.
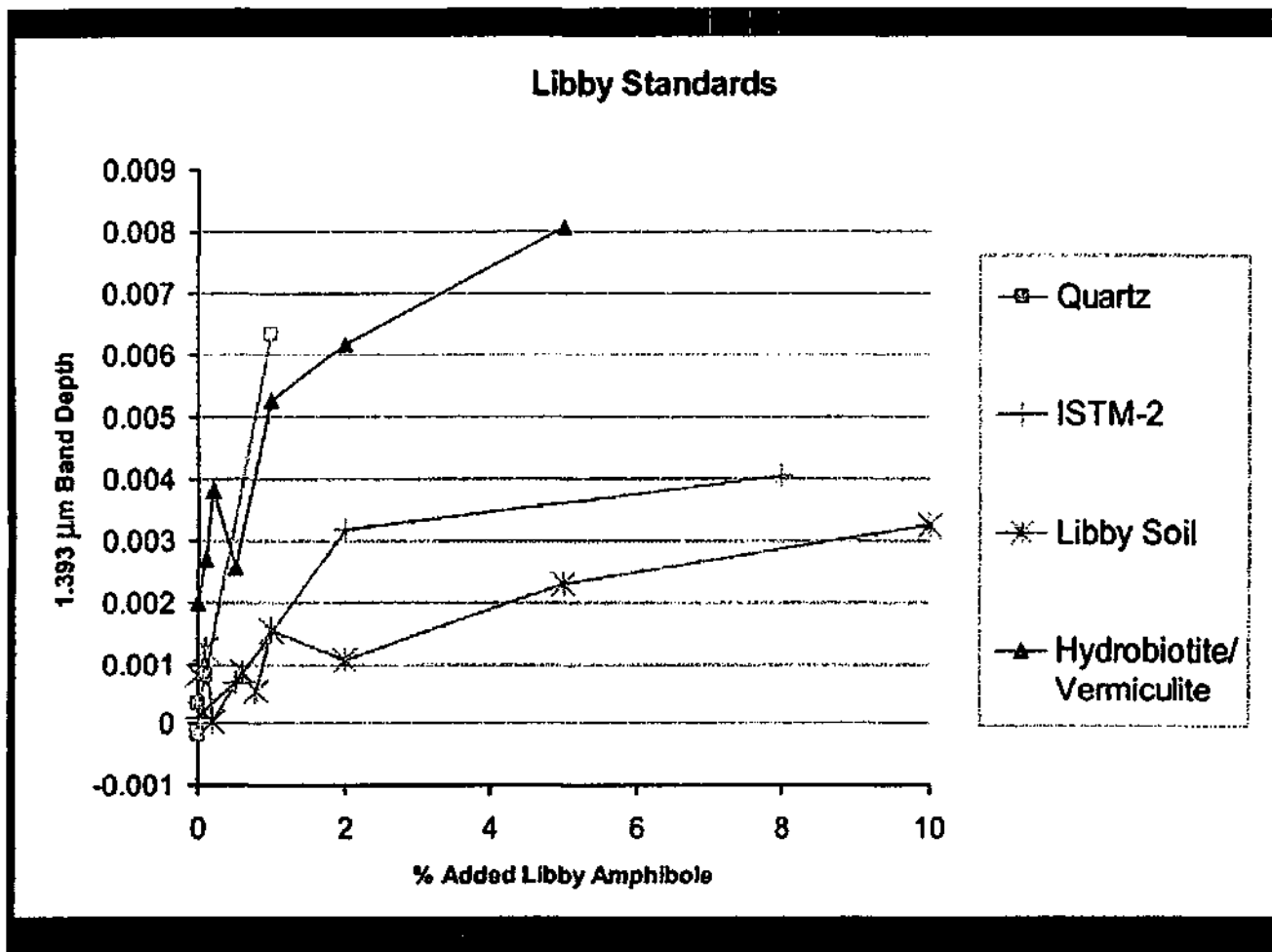
Figure 18. The measured 1.393-micron absorption strength for standard series of Libby richterite mixed with quartz, a Libby soil, the ISTM 2 (Libby soil) series, and ultrasonically-washed vermiculite flakes. Because the grain size and reflectance level of each matrix material is different, different trend lines are observed.
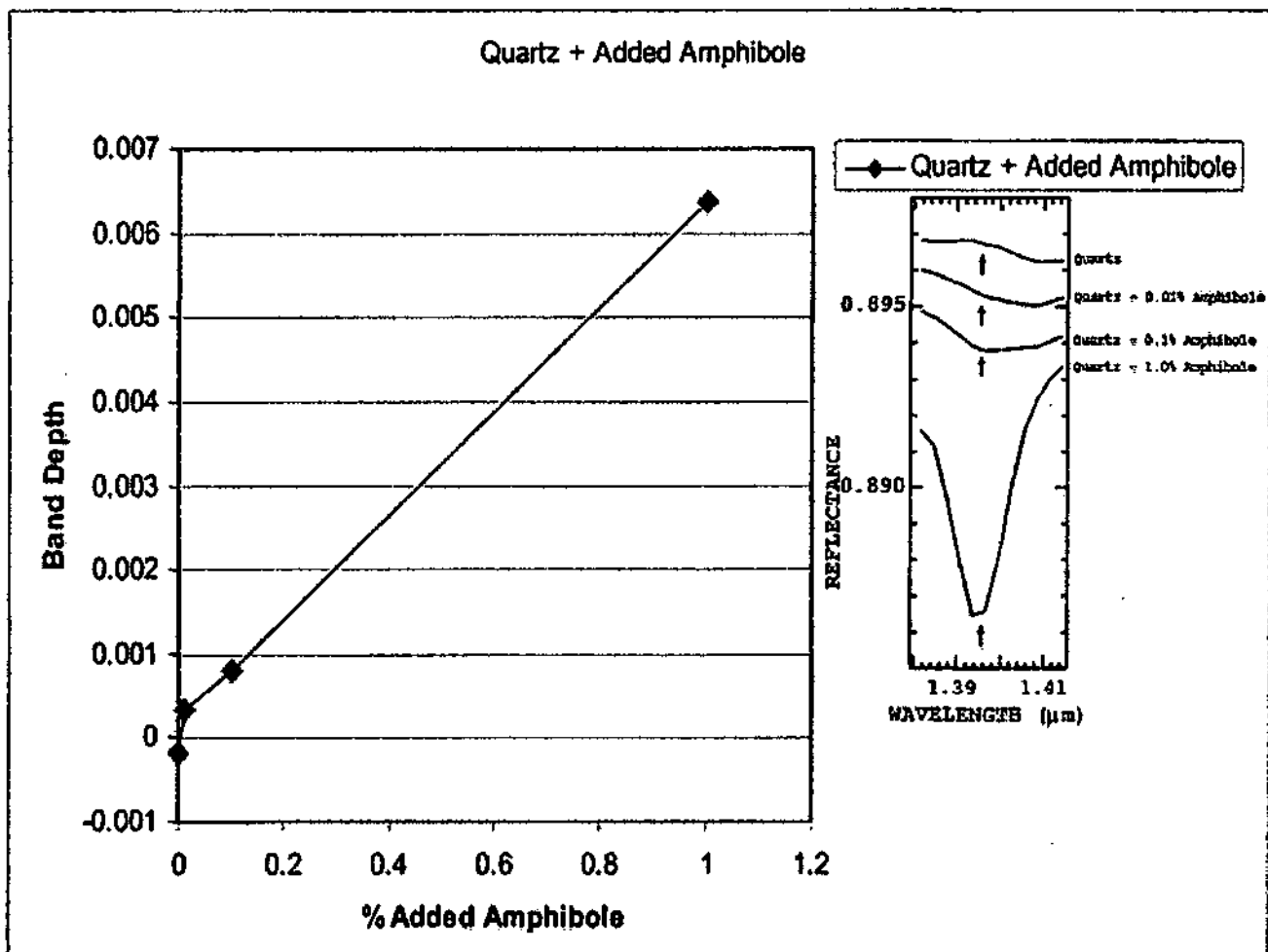
Figure 19. Same data as in Figure 18, but showing lower abundance levels. A mixture of only 0.01 wt % richterite (100 parts per million) produces detectable absorption.
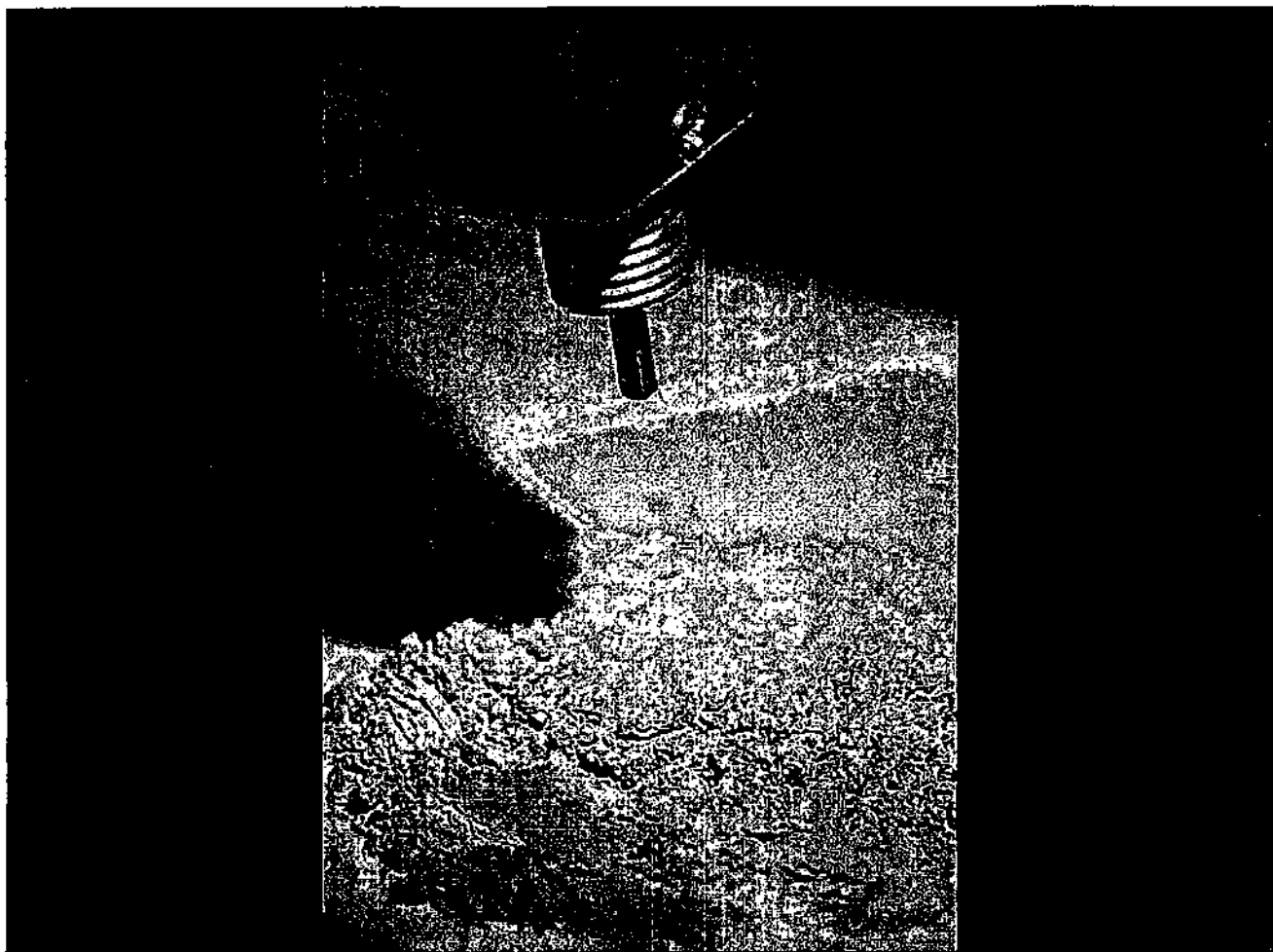
Larger 17 KB image

Figure 20a. ISTM2 sample GS0241 with the spectrometer fiber-optic probe at top. The threaded metal part is 0.5 inch diameter. The field of view on the sample is slightly more than about 1 inch (~ 3 cm). Small white pieces in the sample are Libby fibrous amphibole and the matrix is a typical soil from the Libby area.

ISTM 2 sample GS0241, image stretch to show sample variability
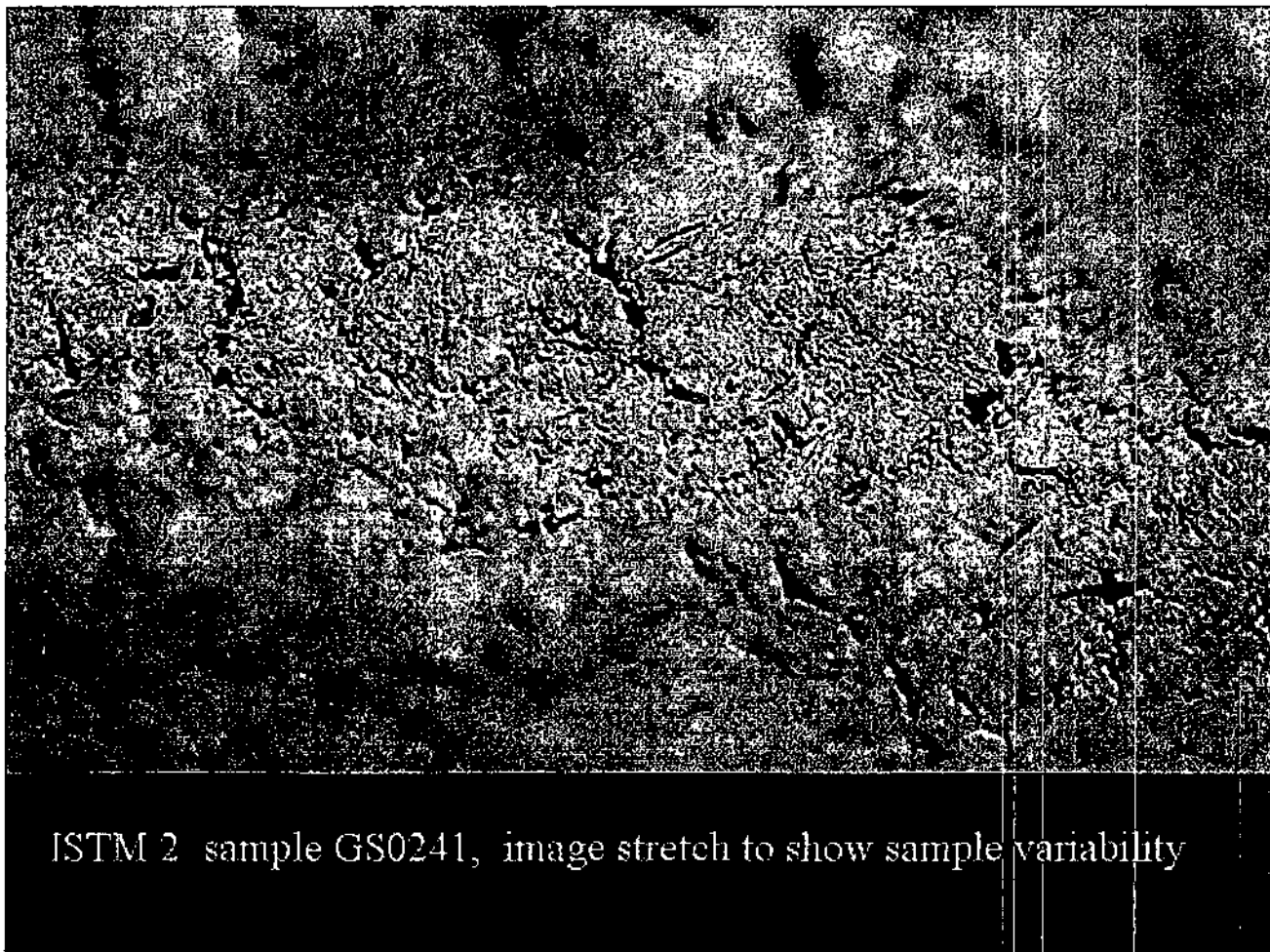
<u>Larger 17 KB Image</u>

Figure 20b. ISTM2 sample GS0241 close-up. Many white pieces in the sample are Libby fibrous amphiboles. The largest one is "pencil-lead size,"

Detection of Fibrous versus non-Fibrous Amphiboles with Spectroscopy

Can spectroscopy be used to tell the difference between fibrous and non-fibrous varieties of amphibole and other minerals? The contribution to absorption bands are usually due to photons traversing all axes of the mineral. A chemical bond will have the greatest influence on absorption when it is perpendicular to the direction of photon travel. If photons are prevented from traversing one or more crystallographic axes, then the absorption from those axes will not contribute to the absorption. This can be done with single crystals and a polarizer, allowing study of each crystal axis. In a normal particulate surface, measured in reflectance, the photon direction is random, so all crystal axes are probed by the photons scattering in the surface. However, photons will have low probability of traversing the long dimension of fibrous crystals. Even the few photons that are oriented to encounter and travel directly along the fiber would preferentially be absorbed because of the much greater path length in the mineral. Thus, one might expect a change in the spectrum of fibrous versus non-fibrous minerals. Either an entire absorption could disappear, or simply the main absorption could appear narrower in width.

We examined a number of amphibole spectra and find that the Libby amphibole has a narrower width of the 1.393-micron OH-stretch overtone absorption than do non-fibrous amphiboles that are close in composition to the Libby amphibole. The effect observed is small, and the spectral bandpass and sampling required is on the order of 0.001 microns. Further study is required to prove and quantify this effect.
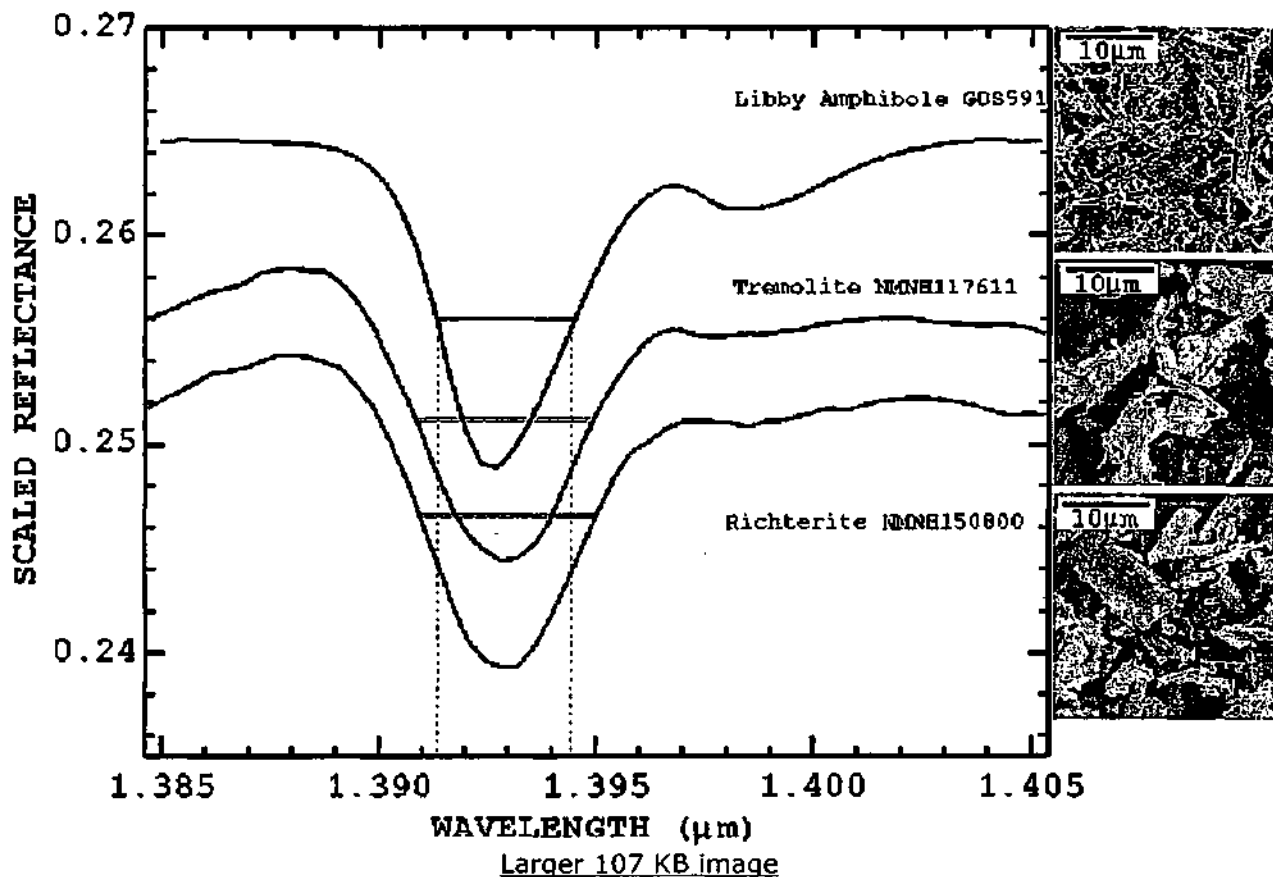
Figure 21. Fibrous versus non-fibrous effects on spectral features. The Libby amphibole is fibrous with fiber sizes typically less than 1 micron (less than the 1.4 micron wavelengths in this plot). The other richterite and tremolite are non-fibrous varieties a coarser grained. The fibrous amphibole has a narrower absorption feature.

Reflectance Spectroscopy - Polarized Light Microscopy Comparison

We compared Reflectance Spectroscopy (RS) to Polarized Light Microscopy (PLM) analyses on natural samples from the Libby region. Samples were collected by the EPA and splits supplied to the USGS for analysis. Other splits were supplied to contractor labs and the data from those labs supplied to us by the EPA. We must note that because of possible sample inhomogeneity due to richterite electrostatic effects, regardless of splitting methods used, the samples may not be exactly identical in richterite content. However, examined as a whole, statistically one would expect similar trends if each method had similar detection levels. We see in Figure 22, however, that spectroscopy seems to detect more cases than PLM. Spot checking some samples in the SEM confirmed some samples that were non-detect by PLM contained richterite, however, time and funding has precluded rigorous fiber counting with TEM or SEM to determine true richterite levels. Statistically, though, from the evidence presented here, spectroscopy should be able to probe into vermiculite grains and detect richterite that would not be seen by PLM.
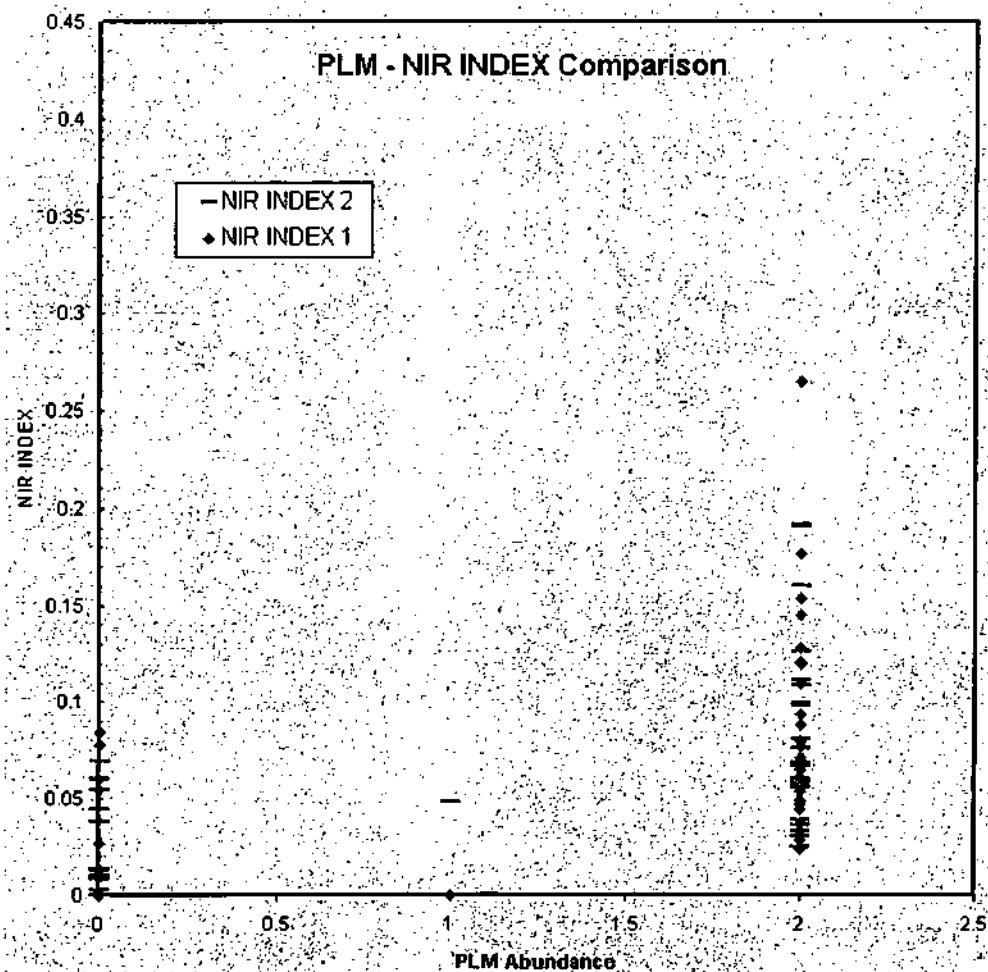
Figure 22. Comparison of absorption strengths observed in reflectance spectra of approximately 180 natural samples from the Libby, Montana region compared to standard Polarized Light Microscopy (PLM) measurements. Note the many non detects by PLM where reflectance spectroscopy detects richterite absorption. The NIR index 1 and 2 are scaled absorption strengths of the 1.393 and 2.31-micron features, respectively.

Effects of Spectral Resolution on Amphibole Detection

So far, we have discussed the spectral properties of the Libby amphiboles using spectra from an Analytical Spectral Devices portable field spectrometer with approximately 0.011 micron (11 nm) spectral bandpass (Full Width at Half Maximum; see Clark, 1999). But the 1.393-micron tremolite-winchite-richterite feature is narrower than this spectral resolution. The natural width of the absorption feature is only about 0.003 micron. A spectrometer with a narrower spectral resolution would be able to see the feature as a narrower line (Figure 23a, 23b) and be able to separate it from other absorptions at lower abundances (Figure 24).

In Figure 24 we see spectra of a mixture of Libby amphibole and Libby soil containing a strong muscovite signature at 2 spectral resolutions. At 0.011-micron resolution, the amphibole does not even produce a local minimum at 1.393 microns. Detection of the amphibole requires accurate definition of the continuum (see Figure 24, top). But at 0.0008-micron resolution, the amphibole produces a local minimum at 1.393 microns showing a readily observable and stronger absorption feature. We estimate amphibole detection should, in general, be improved approximately linearly with improvements in spectral resolution from 0.011 to at least 0.002 micron, or about a factor of 5. Higher resolution, however, may require working in a dry nitrogen atmosphere environment to reduce effects from atmospheric water absorptions.
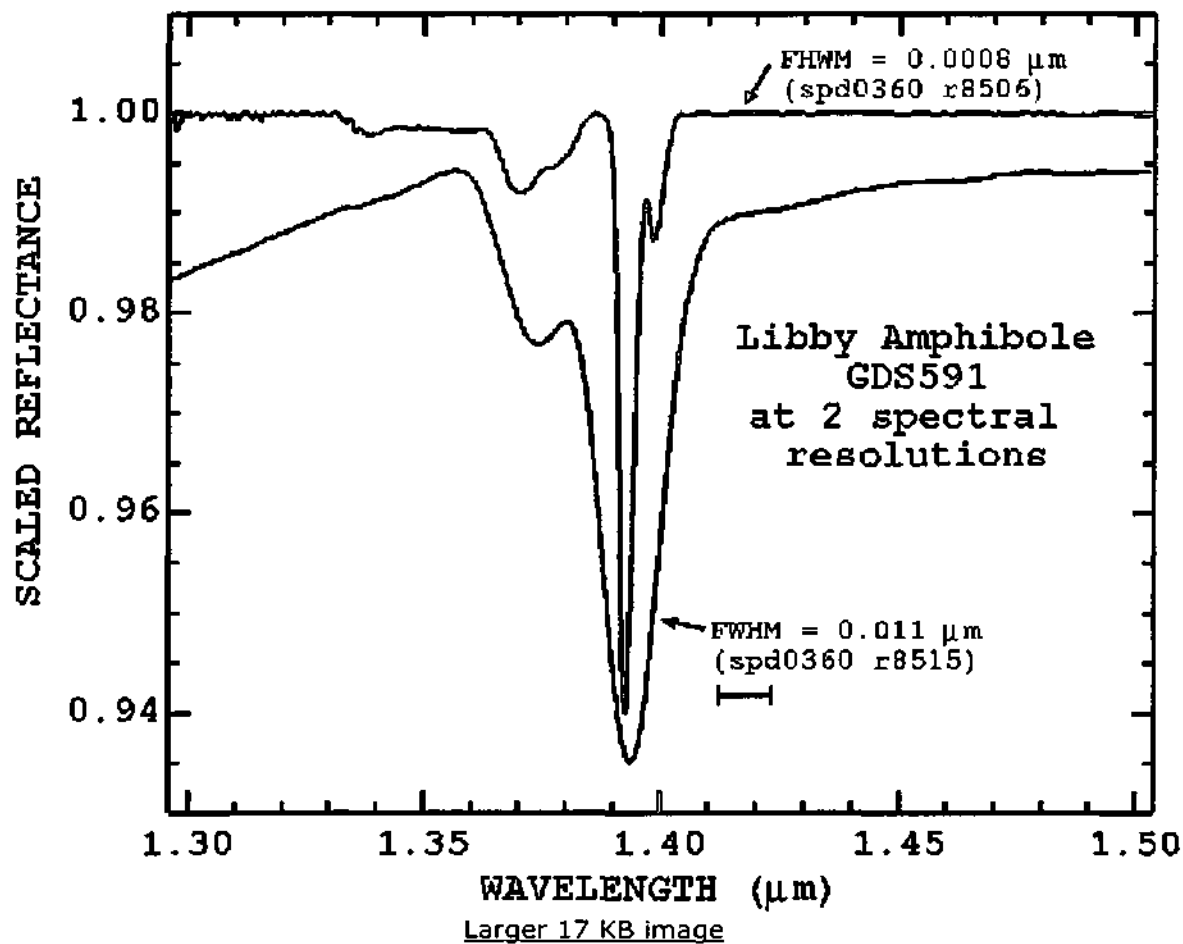
Figure 23a. The Libby amphibole (sample ID= GDS 591) 1.393-micron absorption feature is shown at 2 spectral resolutions.

FHWM = 0.0008 μm
(spd0360 r8506)
H

Libby Amphibole
GDS591
at 2 spectral
resolutions

FWHM = 0.011 μm
(spd0360 r8515)

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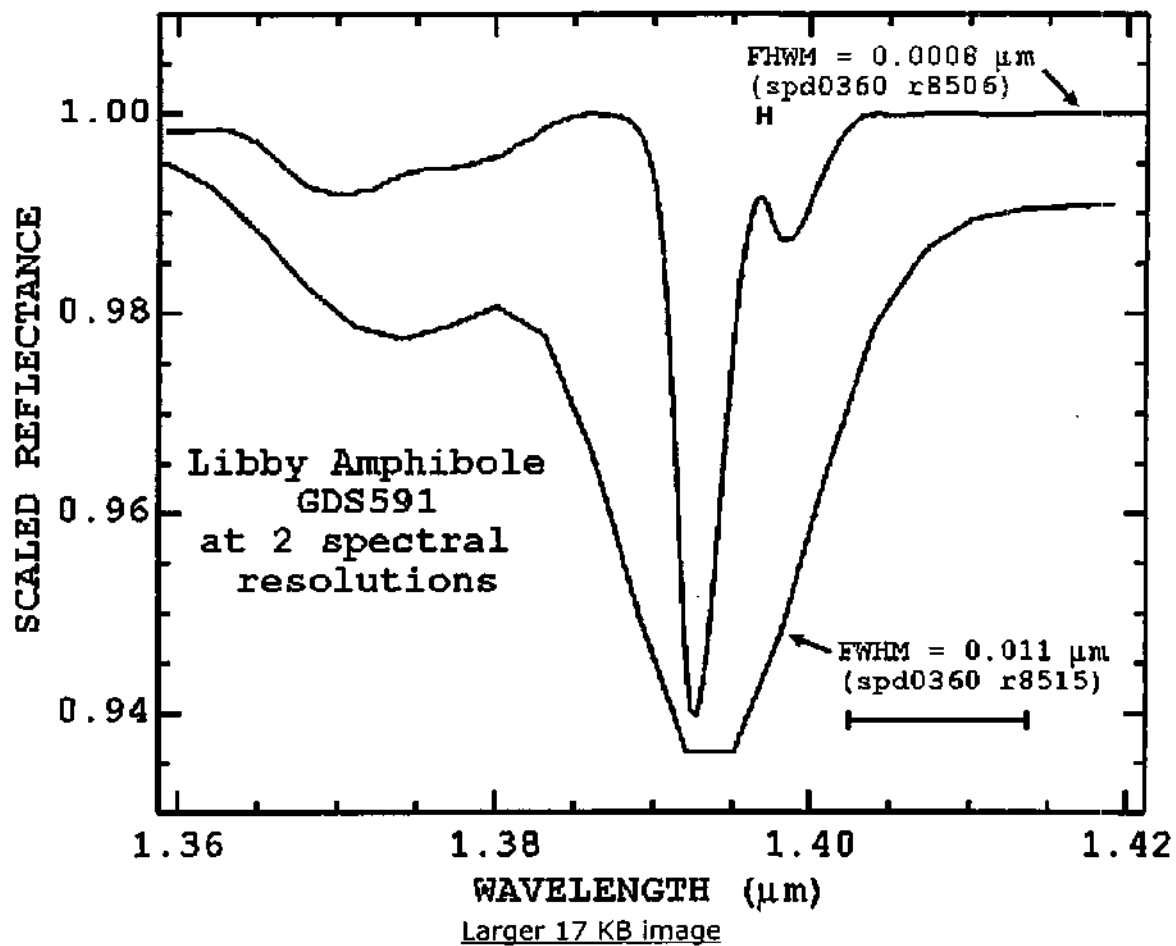
Figure 23b. The Libby amphibole (sample ID= GDS 591) 1.393-micron absorption feature is shown at 2 spectral resolutions. This is the same as Figure 23a, but a closer view to show details.
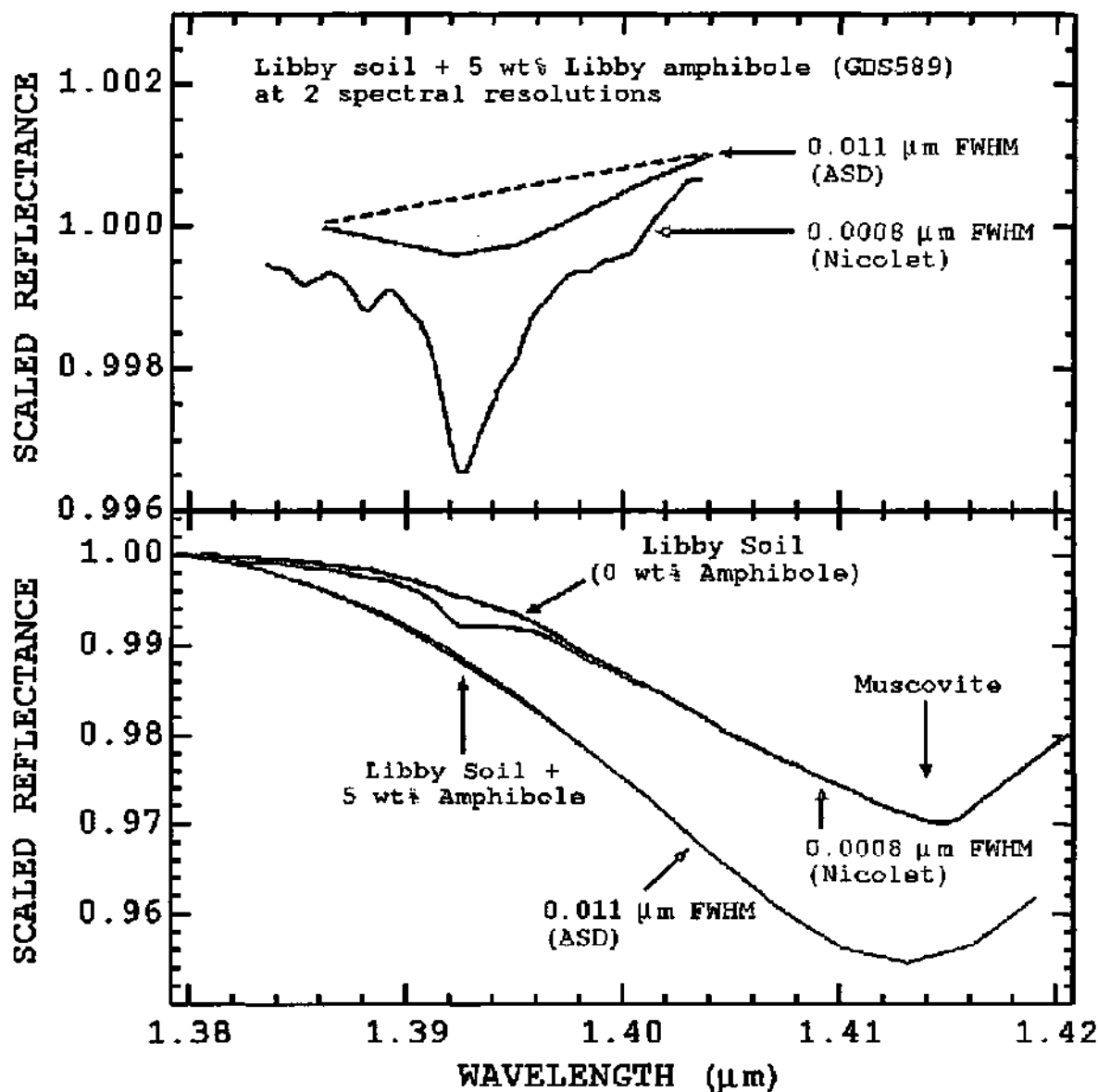
Figure 24. Spectra of a mixture of 5% Libby amphibole and Libby soil is shows at two spectral resolutions (bottom curves). At top is shown the 1.393-micron amphibole absorption, continuum removed. The higher spectral resolution shows the amphibole absorption better.

Conclusions / Discussion

The the Libby, MT amphiboles show unusual electrostatic properties, and large variability in fibrous amphibole concentration in laboratory samples, even in washed and well mixed vermiculite-biotite samples. This variability could pose difficulty in obtaining consistent analysis results concerning amphibole content.

The variability has been observed in near-infrared spectra of Libby vermiculite samples. Other laboratory analysis confirm that this variability is a physical property of the minerals. Ore varies between vermiculite, hydrobiotite, and biotite with variable amounts of fibrous amphibole from grain to grain (from spectroscopy and XRD and SEM). The ultrasonically washed (19 times) ore sample still contains fibrous amphibole based on the presence of spectral features as well as SEM and XRD detections.

Reflectance spectroscopy can detect Libby amphiboles with detection limits near 0.5 wt % amphibole on unprepared samples. In

some samples, those with a weakly absorbing matrix, detection limits are as low as 0.01 wt %, using currently available commercial portable field spectrometers. Increasing spectral resolution (using commercially available laboratory spectrometers) can improve detectability up to about 5 times (0.1 wt % on typical Libby samples and to about 0.002 wt % on weakly absorbing samples).

Reflectance spectra measured on unprepared samples can achieve excellent signal-to-noise ratio in about 0.5 minute. More than 60 samples can be measured per day by a 2-person team (5-minutes per sample), including necessary calibrations. With efficient sample handling, this number can be doubled. Analysis of Libby and World Trade Center samples to date show that reflectance spectroscopy can be an effective rapid screening tool. Reflectance spectra are a digital record of the sample. Thus in the future, better algorithms could be applied to the same data if lower detection limits become important. Analysis can be minimally biased by a human, and, depending on the algorithm, analysis can be automated. reflectance spectroscopy can be deployed in a laboratory, in the field, and from aircraft. As a rapid screening tool, reflectance spectroscopy can reduce analysis loads on more expensive but detailed analyses using the "sieve" analysis methods.

Reflectance Spectroscopy

- Pros:
    - Probes a larger volume of material than other methods.
    - Is non-destructive.
    - No sample preparation necessary.
    - Detection from aircraft, in th the field and in the laboratory.
    - Can obtain spectra in seconds or less on samples from millimeters to meters, providing real-time feedback.
    - Good low level detection limits below 1 wt% for Libby amphiboles in common Libby rocks and soils.
- Cons:
    - Not quantitative (or only semi-quantitative).
    - May not be able to distinguish between fibrous versus non-fibrous richterite at low spectral resolution. (research on this topic still to be done.)

Currently there we know of no commercial algorithms for this analysis. Detection of amphiboles at low abundances may require removal of major components from the spectra. This can be done by a simple ratio method, but the absorption band positions of the matrix material must be matched (Figure 24). Currently we do this as a custom fit using our experience in spectroscopy. A menu driven analysis system could allow an analyst to try different matrix spectra to minimize interference from absorptions in the matrix. The system would show the test spectrum ratioed by the matrix and amphibole spectral regions displayed to show if an amphibole can be detected in the spectrum, as in Figure 24.

Further information on reflectance spectroscopy can be found at: **http://speclab.cr.usgs.gov**.

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FIRSTGOV

Tabbed Page:
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LABORATORY DETECTION AND REPORTING LIMIT ISSUES RELATED TO RISK ASSESSMENTS

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Abstract

"I expected low parts-per-billion reporting limits and got high parts per million, what's wrong with the lab?" This is a statement often heard when the Laboratory Measurement Quality Objectives (MQO) for either a Human Health Risk Assessment (HHRA) or an Ecological Risk Assessment (ERA) are not met, even though the selected analytical method indicated that the compounds should have had reporting limits that were low enough to permit risk assessment. The difference between what the analytical procedure can report for a prepared standard and what is reported for the environmental sample is the difference between ideal and real-world samples. Does this mean it is never possible to achieve MQOs? Not necessarily. However, to do so, it is important to (1) establish specific reporting limit goals, (2) communicate and contractually negotiate those goals with the analytical laboratory, (3) make the laboratory aware that if goals are not being met, actions are to be taken immediately to identify what needs to be done to obtain the required data, and (4) if analytical constraints do preclude achieving the MQOs, be prepared to negotiate alternative screening options with the regulatory agency.

Issue Paper Objective

The objective of this issue paper is to provide an overview of what may be required to achieve data quality objectives. It is not intended to transform its readers into analytical chemists nor to be a definitive set of guidelines that will always get the reporting limits required from the laboratory. Rather, this paper presents a brief discussion of how environmental samples are processed and analyzed, of the terminology typically used during analysis and data reporting, and ways to improve the reporting limits. It also stresses the importance of maintaining close communications with the laboratory so that the lab understands the necessity for achieving data reporting goals and the need to notify the prime contractor/remedial project manager (RPM) as soon as the lab realizes that goals will not be met (rather than waiting until the data report is delivered).

Presented are examples of how reporting limits can be lowered. Although the examples used here are typically for organic compounds in aqueous environmental samples, the rationale is also applicable for other compounds (i.e., inorganics) and matrices (i.e., soils, sediments, and tissue).

In addition, the methods presented in the text generally reflect the most recent U.S. Environmental Protection Agency (U.S. EPA) methods. The use of these methods in no way implies that older versions are no longer appropriate. A high degree of flexibility for method-modification is possible and actually encouraged by the U.S. EPA to achieve detection/reporting goals, as long as valid quality control/quality assurance (QA/QC) policies are applied and documented.

Issue Discussion

1.0 Introduction and Background

Generally, some variance will exist between the lowest concentration that an analytical instrument can detect and the concentration that is reported for an environmental sample. This variance reflects the difference between analyzing a relatively simple laboratory-prepared standard and a complex environmental sample that may contain a substantial difference in concentrations between a standard and the sample.

The laboratory standard normally contains only the compound or compounds of interest, in an optimal calibration range, and in a medium that does not interfere with and can even enhance the performance of the analytical instrument. Under these ideal conditions, the analytical system provides the lowest concentration that can be reported, while minimizing uncertainty due to matrix effects. This concentration is the method detection limit (MDL). On the other hand, an environmental sample may not only contain the compounds of interest in relatively smaller concentrations, but also many nontargeted compounds and other constituents that can interfere with the sample analysis. Any deviation from the ideal laboratory sample results in a method reporting limit (MRL), which is the corrected concentration reportable for that sample under those conditions. The MRL is always equal to or greater than the MDL.

Once the targeted compounds and MQO reporting limits are established by the project team, the appropriate analytical methods are selected that would best address the compounds and the environmental sample matrix (i.e., water, soil, sediment, or tissue). Communicating with the laboratory during the method selection process is advisable so it can be confirmed that they can perform the analysis and meet MQOs. The method that is selected will provide guidance on how to prepare the sample, analyze the sample, and report the concentration of the compounds in the samples within appropriate QA/QC guidelines. It should be emphasized that the commonly used SW-846 methods: (1) are not the only source of methods that can be used, (2) do NOT have to be implemented exactly as written, and (3) performance presented in those methods should NOT be used as a regulatory default or absolute "QC requirements" (Crumbling and Lesnik, 2001).

To understand what causes MRLs to be higher than the MDLs, it is important to have some knowledge of what is involved in processing an environmental sample. Generally, three steps are associated with the analytical process: (1) sample preparation (which can include an extraction and additional preparation of the extract), (2) sample analysis, and (3) raw data reporting (see Figure 1).
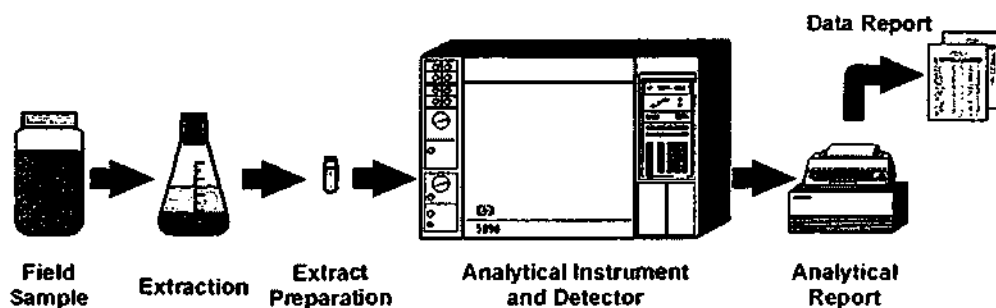
Figure 1. Sample Preparation and Analysis Process

Normally, it is not possible to introduce the environmental sample directly into the analytical instrument. The sample must undergo an extraction step during which the targeted compounds are removed from the environmental matrix (i.e., water, soil, sediments, tissue) and transferred to a secondary matrix (i.e., extraction solvent) that can be introduced into the analytical system. However, one drawback with most extraction processes is that both targeted and nontargeted compounds may be extracted. These extraneous compounds can cause interferences and make it impossible to report concentrations at the originally specified MDL.

When the extract is introduced into the analytical instrument, ideally, all of the compounds associated with that sample need to be separated into discrete bands for optimum detection limit applications. These bands then pass through a detector, which produces an electrical signal that is proportional to the amount of each compound in the sample. All of the detector responses for the sample are compiled in an analytical report that is used to generate the data report.

2.0 Analytical Method Terminology

The following terms are associated with the analytical method and should be understood in order to evaluate analytical and data reports. It is possible that different laboratories may use different terms to describe these same concepts. If the data report contains terminology you do not recognize or understand, contact the laboratory for an explanation and request that information be included in the case narrative.

- Method Blank (MB): The MB contains only the reagents/solvents being used to prepare the sample. The method blank confirms that the analytical instrument is "clean" and that the reagents/solvents are of good quality. If MB data indicate concentrations for any of the compounds associated with the sample, then the laboratory must explain why they were present, and must correct the problem before analyzing the environmental samples.

- Method Detection Limit: The MDL is the sample concentration of each compound that can be detected above zero and with a 99% confidence, when a particular analytical method is employed properly. As an example, in SW-846 Method 8260B (a gas chromatography [GC] analytical method with a mass spectrophotometer detector), the

stated MDL for benzene is 0.03 µg/L for a 25-mL groundwater sample processed with a purge and trap sample preparation by SW-846 Method 5030.

- Practical Quantitation Limit (PQL)/Estimated Quantitation Limit (EQL): PQLs and EQLs are synonymous terms in SW-846 and are the reporting limit provided in the method. They are a guide for the "expected" concentration that can be reliably achieved within specified limits of precision and accuracy during routine sample analyses. The PQL (or EQL) is generally 5 to 10 times the MDL, but highly matrix dependent. As an example, SW-846 Method 8260B provides PQLs for benzene of 1 µg/L for a 25-mL groundwater sample and 5 µg/kg for soils/sediments with low-level contamination. The method also indicates that PQLs are 50 times the MDL for water miscible samples, 125 times the MDL for high concentration soils and sludges, and 500 times the MDL for non-water-miscible waste. These multipliers are typically associated with dilution factors.

- Method Reporting Limit: The MRL is the lowest reported concentration, provided on the sample-analysis data report, after corrections have been made for sample dilution, sample weight, and (for soils and sediments) amount of moisture in the sample. MRLs can be as low as the MDL or exceed the PQL, depending on the matrix effects encountered during the analysis. **The MRL is the value that indicates whether the analytical MQOs have been achieved for that sample.**

- Precision: A QA/QC function that quantifies a laboratory's ability to generate reproducible data, for multiple analyses of the same sample. It does not assume knowing the true concentration in the sample. Precision is expressed as a relative standard deviation (RSD) and is compared to the RSD provided in the analytical method. If the reported precision deviates from the laboratory's specified acceptable range, then validity of the data may be compromised. In SW-846 Method 8260B, benzene's RSD is ~3%, depending on the sample matrix.

- Accuracy: A QA/QC function that quantifies a laboratory's ability to generate data that is in agreement with the true concentration or a reference value. In this case the true concentration is known. Accuracy of 100% indicates that the reported value is equal to the true concentration. The range of acceptable accuracy and precision is provided in the method or established through statistical procedures by the laboratory for each matrix. If accuracy and precision do not meet the guidelines, then the usefulness of the data is questionable. For example, in SW-846 Method 8260B, a measure of acceptable accuracy for benzene in water is a spike recovery of 80% to 120%.

For risk assessments, the data being reported and subsequently used must be of the highest quality and certainty. The relationship between the method blank, MDL, limit of quantification (further discussed in Section 3.2), and the certainty associated with the measured concentration of the analyte is presented in Figure 2. The laboratory should be reporting data where the analytical concentration of the compound is in the region of high certainty.
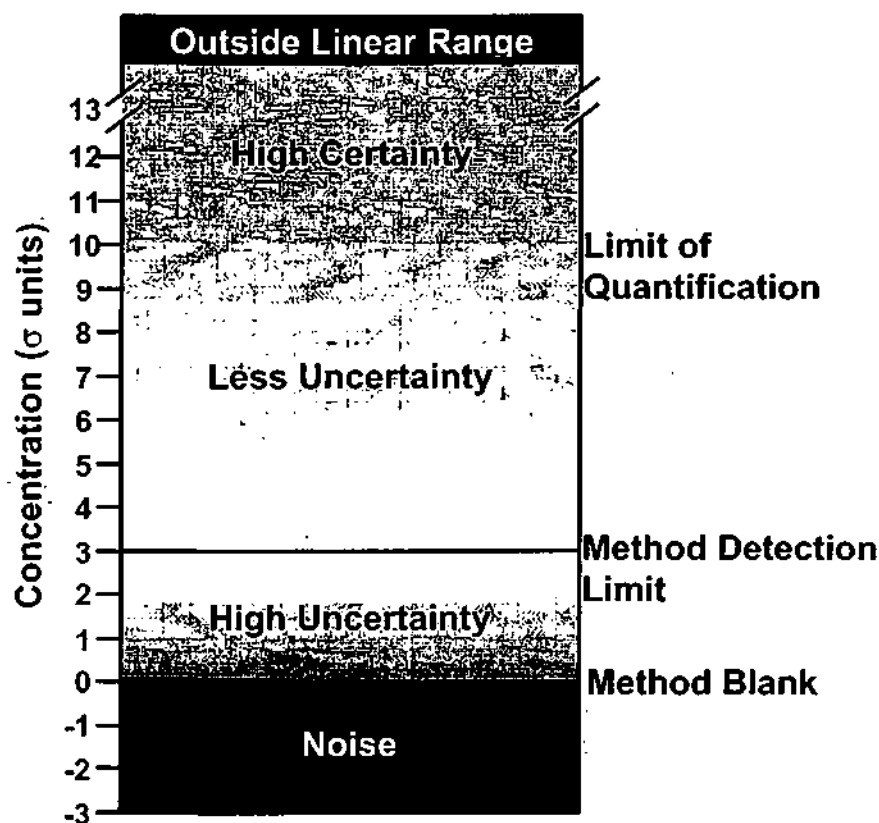
Figure 2. Analyte Concentration vs. Reporting Certainty. (The y axis represents signal strength, in units of the standard deviation (σ) used to determine the MDL.) Adapted from Keith, 1991 by Johnson, 2001.

3.0 Factors Affecting Method Reporting Limits

What prohibits achieving reporting limits at the MDL for all samples? Two factors that can significantly increase the reporting limit are matrix effects (i.e., bulk effects and coextractants) and the dilution of samples.

3.1 Matrix Effects

If the sample matrix possesses properties that affect the detection of a particular analyte, then it is said to be causing interference. A matrix spike is the QA/QC activity used to determine if a sample is providing any interference. When a sample is spiked, a known concentration of a targeted compound is carefully added to the sample, similar to a QA/QC accuracy analysis. The spiked sample is analyzed and the recovery percentage is calculated by comparing the reported

concentration of the compound before and after the spike. If the recovery is higher than the acceptable upper limit, then the matrix may be providing an additive effect and reported values could be higher than what is in the sample (Type I Error). If recovery is below the acceptable lower limit, then the sample matrix may be masking that compound and the reported data could be lower than what is actually present in the sample (Type II Error). Additional sample extract preparations can be performed that may negate matrix effects by removing the interfering compounds. However, extreme care must be taken during extract preparations since extraction efficiencies are never quantitative, and extraction effects can increase the uncertainty of the analytical measurement.

3.2 Dilution Factors

No laboratory activity can have a more dramatic effect on MRLs than the dilution of a sample. The more a sample is diluted, the higher the reporting limit automatically becomes. As an example, if the laboratory dilutes a sample tenfold (meaning one volume of the sample is added to nine volumes of a solvent), and the target MDL for the analyte is 1 part per million (ppm), then the reporting limit automatically increases by a factor of 10 and becomes 10 parts per million.

Why is it necessary to dilute a sample? An analytical detector is limited not only by the smallest amount of material it can respond to, but also by a maximum amount of signal per unit concentration of the sample. The lowest concentration, reported with high certainty, is the limit of quantification, and the highest concentration is called "full-scale response". Acceptable performance for a detector falls between this low- and full-scale-response loading. Optimal performance occurs when there is a linear increase in detector response versus a compound's concentration. That is, if a compound's concentration is doubled, the signal from the detector also would double. It is within this range of linearity-of-response that a detector is typically calibrated and operated.

Therefore, sample dilution is required when the concentration of a compound exceeds the amount that produces a full-scale response. At that point the detector becomes saturated and fails to respond to any additional material. During saturated conditions, the detector also can become contaminated and require extensive cleaning and conditioning in order to recover its linearity-of-response for later analyses. This results in downtime for the instrument and loss of sample throughput for the laboratory.

Normally, if a target compound has a very high concentration and it requires dilution, there should be little concern about the MDL because the concentration is well above its detection limit. In this case dilution is necessary to bring the measured concentration within the optimal calibration (measurement) range. Dilution impacts screening values when the compound's concentration in a sample is close to or at the MQO level, but there are several other nontarget analytes at very high concentrations. Any dilution of the sample to accommodate the high concentration of nontarget analytes may reduce the concentration of the target analyte to a level where it can no longer be detected.

It is a common practice for the analytical laboratory to screen the sample extracts on an instrument that is not used for data generation. Based on the results of that injection, the decision is made by the laboratory as to whether a sample requires dilution.

3.3 Data Flags

The laboratory must flag any data associated with low or high matrix-spike-recovery issues or other abnormal analytical conditions that deviate from stated method procedures. QA/QC deviations must be communicated to the RPM/Comprehensive Long-Term Environmental Action Navy (CLEAN) contractor as soon as they are observed so that data quality can be immediately assessed. Table 1 provides a list of commonly used data flags and their effects on data quality.

Table 1. Data Qualifier Flags*

Flag	Description	Does it Compromise the Utility of the Data?**		
		Yes	No	Maybe
B	Compound was detected in the method blank. Indicates possible/probable blank or system contamination and warns the data user to take appropriate action.			X
C	Pesticide results where the identification has been confirmed with gas chromatography-mass spectrometry (GC-MS).		X	
D	Compound was detected in an analysis performed at a secondary dilution.		X	
E	Reported value is either an estimate or it exceeded the linear range of calibration. An explanatory note must be provided by the laboratory.	X		
F	Analyte was positively identified, but the reported value is below the PQL.			X
J	Compound was detected, but below the specified reporting quantification limit. Any such reported amount should be considered an estimate.			X
M	Duplicate injection precision not met. Can also mean matrix effect was present.	X		
N	Spiked sample recovery not within control limits.	X		
Q	No analytical result.	X		
R	Quality control indicates that the data are not usable (compound may or may not be present). Resampling and reanalysis are necessary for verification.	X		
S	Reported value was determined by the Method of Standard Addition.			X
	Can also mean it was a saturated peak.	X		
T	Tentatively identified compound (using GC-MS).			X
U	Compound was analyzed for but not detected at or above the specified reporting limit.			X
X,Y,Z	Other specific flags (laboratory defined) required to properly define the results.			X

* Note: flag descriptions may vary between laboratories; therefore, the use of qualifiers should be well defined on each data report.
**Final designations are dependent upon the specific cause of the qualifier.

4.0 Options for Lowering Reporting Limits

The U.S. EPA not only allows but encourages method modifications in order to meet reporting requirements. As stated by Crumbling and Lesnik (2001), "EPA policy in the waste programs is that analyses are required to 'get the right answer' as demonstrated by the quality assurance mechanisms. If an accepted method cannot 'get the right answer' due to analytical difficulties

with the matrix, etc., selection of a different method, or modification of a method is required". It should be remembered that modifications to existing methods must be done with the approval of the regulator and should be addressed in the Quality Assurance Project Plan (QAPP). Additionally, any extra efforts to lower reporting limits will likely result in higher analytical costs.

Options exist that can enhance an analytical method and possibly permit lower reporting limits, and these tools should be employed to accomplish analytical goals. However, in order for the RPMs/CLEAN contractors to know that these or other options are needed, the laboratory must contact them when the screening process indicates MQOs are not going to be met. This requires good lines of communication to be established between lab/CLEAN/RPM prior to any samples being submitted for analysis.

During contractual negotiations with the laboratory, a request should be made for them to provide detailed information on how they intend to prepare and analyze the samples. Options that are available in the lab for sample cleanup, to enhance reporting limits, should also be identified. This should be established prior to any samples being sent to the lab.

4.1 Option 1: Adjust the Analytical Injection Volume or Reduce the Dilution Factor

One way of lowering the reporting limit is to deliver more of the targeted compound to the detector. This can be accomplished by either introducing a larger injection volume into the analytical instrument or by preconcentrating the sample before it is injected. However, the analyst must keep in mind that coextracted interferences may be present, and unless they are removed, the interfering signal response will increase as well, resulting in no net gain. Therefore, a balancing act exists when increasing the analytical injection volume or concentrating a sample. To make adjustments to the sample concentration, it may require a second extraction/preparation step for the environmental sample. Generally, a 500-g soil/sediment sample will provide more than enough material for multiple analyses. The CLEAN contractor should request information from the analytical laboratory on the volume and the number of bottles required to perform multiple aqueous analyses. Collecting additional material during the initial sampling effort, in case a second extraction/preparation step is required, could prevent the need for costly resampling.

4.2 Option 2: Sample Preparation Alternatives

Another option for lowering reporting limits is to separate the targeted compounds from nontargeted compounds. This procedure can substantially reduce problems associated with matrix interferences and the need for a dilution step. Sample preparation options also make it possible to preconcentrate a sample by reducing a large sample volume, which is too large to inject, down to a smaller volume (the opposite of dilution). The preconcentrated sample, which now contains a greater amount of the targeted compound per unit volume, is then injected. This may dramatically lower reporting limits, if matrix interferences are not present or if they can be subsequently removed. There are several sample preparation methods found in the EPA SW-846

3000 Series Methods. It should be emphasized that the performance of most cleanup procedures is not particularly complicated or expensive for the laboratory to perform. The key factor is working with an experienced chemist who is capable of determining what matrix effects are occurring and which cleanup procedure will be effective. Selected methods for organic cleanup/extraction are presented in Table 2. This table does not provide a complete summary of cleanup/extraction options, but provides examples of what types of options exist.

Enhancement by these and other sample preparation techniques has been investigated (NOAA, 1993 and 1998). During a Naval Facilities Engineering Activity Chesapeake (EFA Ches) investigation of sediment contamination at Mattawoman Creek, NSWC Dahlgren, standard methods were applied. However, to attain very low MRLs, larger than normal sample volumes were extracted, with extreme care being taken to maintain complete recoveries. Multiple cleanup steps then were applied to the extracts to exhaustively remove interferences and, whenever possible, the extracts were reduced in volume to concentrate the targeted compounds. With these extra steps, reporting limits that were close to the MDLs were achieved. Increased costs (i.e., ~50% higher) were associated with the laboratory work, but the costs were justifiable to obtain the required critical measurements. In this study, additional time was required to identify laboratories that could provide these types of custom service and negotiate costs. However, the ERA/MQO goals were met.

4.3 Option 3: Use an Alternate Detector

Just as additional sample preparation efforts can enhance reporting limits, it may be possible to achieve lower reporting limits by using a more sensitive or selective detector. However, the use of alternative detection methods will require consultation with an experienced chemist and the lab that will be doing the analysis.

In Table 3, examples of the characteristics of detectors commonly used during organic and inorganic analyses are presented. The selection of an alternate detector is within the guidelines of standard methods and can provide greater sensitivity while "ignoring" nontarget analytes and interferences. This change may make the difference in whether or not the MQOs are met.

As with other aspects of the analytical method, it is advisable to discuss detector options with the prime contractor/laboratory. For organic compounds, several detectors can be used. However, in most cases the GC-MS instrumentation will provide definitive analysis at the highest degree of sensitivity, with the lowest reporting limit, at a reasonable cost. Similarly, for inorganic compounds, several detector options exist. The inductively coupled plasma-mass spectrometry (ICP-MS) detector, however, permits the screening of multiple analytes in a single analysis, provides high sensitivity, low reporting limits, and the per-analyte cost is comparable to other detectors.

Table 2. Examples of Organic Sample-Preparation Alternatives (not intended to be an all inclusive list)

Method Number	Method Title	Description	Advantages	Disadvantages
Method 3510C	Separatory Funnel Liquid-Liquid Extraction	Serial extraction of aqueous samples with methylene chloride in a separatory funnel.	Extract is suitable for cleanup steps to remove interferences and through preconcentration, possibly lower MRLs.	Moderately labor intensive, requires careful attention to ensure complete recoveries.
Method 3520C	Continuous Liquid-Liquid Extraction	Specialized glassware permits the automatic extraction of aqueous samples with an organic solvent for 18-24 hours.	Minimal manual effort, very effective extraction method, and it generates an extract that is suitable for cleanup and preconcentration.	Decomposition of some analytes (organochlorine pesticides, phalate esters, and phenols) may occur under high pH (basic) extraction conditions.
Method 3535	Solid-Phase Extraction (SPE)	Uses commercially available preparation columns/discs to remove interferences.	Fast, can be used to preconcentrate samples and possibly lower MRLs.	Additional analytical costs.
Method 3540C	Soxhlet Extraction	Specialized glassware permits the automatic extraction of soils and sediments over several hours.	Very thorough extraction and produces an extract suitable for cleanup and preconcentration.	Fritted glassware may be difficult to clean and cause contamination problems for later samples.
Method 3545	Pressurized Fluid Extraction (PFE)	Uses elevated temperature and pressure to accelerate the extraction of soils, clays, sediments, sludges and solid wastes.	Extraction completed in minutes instead of hours.	Method has been validated for pesticides, herbicides, and semivolatile organics at moderate to high parts per billion concentrations.
Method 3610B	Alumina Cleanup	Used to separate analytes from interfering compounds of different polarity.	By adjusting pH, interfering compounds can be selectively removed.	Can cause chemical reactions that may affect certain target compounds. Additional costs.
Method 3620B	Florisil Cleanup	Used to remove interferences from pesticide residues, chlorinated hydrocarbons, and PCB samples.	Can permit sample concentration and lower MRLs.	Requires more time and will result in additional costs.
Method 3630C	Silica Gel Cleanup	Column cleanup of sample extracts with polyaromatic hydrocarbon (PAH), organic pesticides, and polychlorinated biphenyls (PCBs).	Can permit sample concentration and lower MRLs.	Requires more time and will result in additional costs.
Method 3640A	Gel-Permeation Cleanup	Compounds are separated based on their molecular size.	Effective at eliminating matrix interferences from sulfur, humic/fulvic compounds, and petroleum organics.	Requires skilled analysts and special instrumentation. Results in a dilution of the sample, which may hinder achieving DQOs. Additional costs.
Method 3650B	Acid-Base Partition Cleanup	A liquid-liquid partitioning process, separates acid from base-neutral analytes.	Can reduce interferences associated with petroleum wastes.	Requires more time and will result in additional costs.
Method 3660B	Sulfur Cleanup	Removal of sulfur interferences from sediment samples.	Can enhance performance of selected detectors.	Requires more time and will result in additional costs.

Table 3. Examples of Analytical Detectors Options

Detector	EPA Methods	Sensitivity	Advantages	Disadvantages
Organic Analysis Detectors				
Flame Ionization Detector (FID)	Methods 8015, 8030, 8040, 8100. Volatile, semivolatile, and high molecular weight organic compounds.	Can report parts per billion concentrations for high molecular weight compounds.	Responds to many compounds and displays a very wide range of linear responses.	Lacks specificity, therefore it can provide false positives in complex samples.
Electron Capture Detector (ECD)	Methods 8060, 8080, 8090, and 8120. Chlorinated solvents and pesticides.	Extremely high sensitivity (parts per trillion) for halo-genated compounds.	Does not respond well to hydrocarbons, so it can negate some interferences.	Narrow range of linear responses and easily contaminated.
Photoionization Detector (PID)	Methods 8020, 8021, 8021B. Responds to benzene, toluene, ethylbenzene (BTEX), PAHs, and some solvents.	Detection limits to parts per million levels.	Does not respond well to aliphatic hydrocarbons, so it can negate some interferences.	Fairly narrow range of linear responses, can become contaminated and require physical cleaning.
Flame Photometric Detector (FPD)	Methods 8140, 8150. Detects organo-phosphorous pesticides.	Detection limits to parts per billion levels.	Can be operated in a phosphorous mode, which negates interferences.	Relatively narrow range of linear responses, sulfur provides a severe interference.
Mass Spectrophotometer Detector (MSD)	Methods 8260, 8270, 8275, 8280, 8290. Volatile and semivolatile organic compounds.	Detection limits to parts per trillion levels for some organic compounds.	Provides definitive identification, good linearity of response, can identify "unknown" peaks.	Can be overloaded, requires high level of user expertise, typically more expensive analysis.
Inorganic Analysis Detectors				
Flame Atomic Absorption Spectrometry (FLAA)	7000 Series Methods Metals and elemental inorganics.	Detection limits in low parts per million for single element analyses.	Relatively free of spectral interferences, low cost.	High reporting limits and prone to chemical interferences.
Inductively Coupled Plasma (ICP) – Atomic Emission Spectrometry	Method 6010B. Metals and elemental inorganics.	Detection limits matrix dependent, typically lower than FLAA.	Permits simultaneous or rapid sequential analysis of many elements. Relatively free of chemical interferences.	Analyte cost may be slightly higher than FLAA.
Graphite Furnace Atomic Absorption (GFAA)	7000 Series Methods. Metals and elemental inorganics.	Typically, parts per billion detection limits. Can be reduced to sub-parts per billion through sample-preconcentration efforts.	Can provide high sensitivity for single elements.	May not be applicable for all Resource Conservation and Recovery Act (RCRA) and Priority Pollutant Metals, very sensitive to matrix effects, higher cost than FLAA or ICP. Single element sequential analysis.
Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)	Method 6020. Metals and elemental inorganics.	Parts per trillion detection limits.	Monitor multiple analytes in a single analysis, higher sensitivity than FLAA, GFAA, or ICP.	Susceptible to interfering ions.
Ion Chromatography (IC) with a Conductivity Detector	Method 9056 for non-metallic inorganic compounds.	Parts per billion detection limits.	Monitor multiple anions in a single analysis.	Susceptible to interfering ions.

5.0 Using Nondetect Data in Risk Assessments

When an environmental sample is analyzed and a target compound is not detected or the detector signal is less than that required for definitive confirmation, the compound may be reported as "nondetect" (ND) or "U" flagged. There are decisions to be made when reporting ND data and the choice selected will have an impact on the MQOs.

5.1 Options for Reporting ND Data

If an analyte is indicated as a nondetect in the laboratory report, several quantitative values can be applied to that compound for screening purposes. It is recommended that the approach(s) to be used for ND data be negotiated with the regulators and documented as part of the MQO process and during the work plan development.

1. Nondetect = value for the MRL. This assumption is the most conservative for a risk assessment, because it will tend to bias data on the high side. When this approach is used, there is a high degree of confidence that the analyte is probably present, but at a level that is at or just below the MRL.

2. Nondetect = value of 0, indicating that the analyte is absent. This assumption is a nonconservative approach because it potentially will bias data on the low side. Assigning a value of 0 may be acceptable if it is highly unlikely that the analyte is present in the sample. An example would be the case for background samples where there is no history of the target analyte being detected.

3. Nondetect = "no value" given. This is different than providing a value of "0" in as much as a "0" value does have meaning if a statistical analysis of the data is performed. The "no value" approach is also a nonconservative approach.

4. Nondetect = value that is ½ MRL. This is a "middle-of-the-road approach" where it is possible that the analyte would be detected in the sampling location and it "could be" as high as ½ MRL.

5. Nondetect = value that is the percentage of NDs in a data set multiplied by the MRL. This is a statistical approach that takes into consideration the number of ND reports in relation to the overall number of data points in the data set. As an example, if there are 25 ND values in a data set of 100 samples, then 25% of the data were NDs. Therefore, 25% of the MRL would be the value given to ND data.

5.2 Decision Path for Assigning a Value to ND Data

How nondetects are treated will impact risk estimates. The following decision path can be used to assign a value to ND data.

- Does the substance pose a significant health or ecological risk at the MDL? If it does, then a more conservative reporting approach would be justified. If it does not pose a significant risk, then one of the less conservative reporting options could be used.

- Is it reasonable to think that the substance is present in the sample (is it in other site media, was it taken downgradient from detectable concentrations, are there chemical/physical considerations, and are other compounds typically associated with the targeted compound present)? If it is, then using ½ MDL may be the appropriate value.

Interpretation of the ND data should be decided and negotiated when MQOs are established early in the HHRA and/or ERA process.

6.0 When Screening Levels are not Achieved

If MRLs are not low enough to perform the screening HHRA/ERA (i.e., when the MRL exceeds the HHRA/ERA screening concentration for a compound), then those compounds are usually carried forward to the baseline risk assessment. The goal should be to collect the proper data to eliminate as many compounds as possible during the screen. This can be done best by aggressively working with the analytical laboratory to achieve the MQO reporting limits. Detailed guidance for calculating site-specific screening values is presented in the HHRA and ERA web guidance.

There undoubtedly will be cases when it is not possible to achieve all of the screening levels for an HHRA and/or ERA. If it can be communicated to regulators that analytical options were exhausted within the available funding, then it may be possible to obtain adjustments to the MQOs. One option is to use alternative screening values (for example, substituting plant values for invertebrates). By doing so, it then may be possible to perform the risk assessment with existing data.

Conclusions/Summary

In conclusion, options exist to enhance the utility of data relative to detection and reporting limits. Efforts must be made to ensure that the reporting limits meet the required MQOs and therefore allow the RPM to make risk-based decisions. At a minimum, the following items need to be addressed and considered by the RPM in conjunction with the CLEAN Contractor:

1. Clearly define the MQOs and contractually negotiate meeting these goals with the analytical laboratory before sampling activities begin.

2. Examine the methods that are being recommended. Bring the lab in early in the process and always ask the laboratory if the reporting limits can be lowered by

employing an alternative sample extraction technique, performing cleanup steps on the extract, or by using a different analytical detector. Identify what the cost will be for these additional efforts.

3. If possible, obtain historical chemical-analysis data for the site, or sites with similar characteristics, to determine if there have been problems achieving specific reporting levels for the targeted compounds.

4. Get involved in the establishment of the MQOs/QAPP to ensure that options are clearly identified up front if the screening MRLs cannot be achieved. Have these options well defined in the Final QAPP.

5. Have clear decision paths for how to report NDs and what to do when reporting limits are greater than the screening values.

Always be prepared to consult a chemist for specific options. Options are usually available, but they normally come at a cost, and it is the responsibility of the RPM to evaluate whether the extra efforts are worth the cost. Obtaining detection and reporting limits that achieve MQOs and meet risk-assessment needs are possible, but must be diligently pursued to prevent generating unusable data sets.

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Acronyms and Abbreviations

BTEX	benzene, toluene, ethylbenzene and xylenes
CLEAN	Comprehensive Long-Term Environmental Action Navy
ECD	electron capture detector
EQL	estimated quantitation limit
ERA	ecological risk assessment
FID	flame ionization detector
FLAA	flame atomic absorption spectrometry
FPD	flame photometric detector
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry

GFAA	graphite furnace atomic absorption
HHRA	human health risk assessment
IC	Ion Chromatography
ICP	inductively coupled plasma
ICP-MS	inductively coupled plasma-mass spectrometry
MB	method blank
MDL	method detection limit
MQO	measurement quality objectives
MRL	method reporting limit
MSD	mass spectrophotometer detector
ND	nondetect
NOAA	National Oceanic and Atmospheric Administration
PAH	polyaromatic hydrocarbon
PCB	polychlorinated biphenyl
PFE	pressurized fluid extraction
PID	photoionization detector
ppm	parts per million
PQL	practical quantitation limit
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RPM	remedial project manager
RSD	relative standard deviation
U.S. EPA	U.S. Environmental Protection Agency

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Composition, $Fe^{3+}/\Sigma Fe$, and crystal structure of non-asbestiform and asbestiform amphiboles from Libby, Montana, U.S.A.

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ABSTRACT

Compositional data and $Fe^{3+}/\Sigma Fe$ ratios obtained by electron microprobe and Mössbauer analyses are given for a suite of three amphibole and amphibole-asbestos samples collected from the former vermiculite mine near Libby, Montana. A crystal structure analysis, compositional data, and $Fe^{3+}/\Sigma Fe$ values for two samples from a previous study are also reported. The results confirm the conclusion drawn in the previous study that these amphiboles are dominantly compositions ranging from winchite to richterite. Mössbauer spectroscopy yielded $Fe^{3+}/\Sigma Fe$ ratios from 58% to 72% for the five samples.

The crystal structure was determined for a single crystal selected from a bulk sample. Its formula (as determined by electron microprobe analysis and Mössbauer spectroscopy) is $(K_{0.19}Na_{0.32})_A(Na_{0.85}Ca_{1.12}Mn_{0.03})_B(Mn_{0.01}Mg_{4.43}Fe^{3+}_{0.34}Fe^{2+}_{0.19}Ti_{0.01}Al_{0.02})(Al_{0.03}Si_{7.97}O_{22})(OH_{1.63}F_{0.37})$. The refinement was carried out based on space group $C2/m$, with $a = 9.879(2)$, $b = 18.024(3)$, $c = 5.288(1)$ Å, $\beta = 104.377(3)°$ and using data collected at room temperature. Mg is partitioned among the M1, M2, and M3 sites. All of the Fe^{3+} occupies M2, while Fe^{2+} is split between M2 and M3; Ca and Na fill the M4 site, while Na and K occupy the partially filled A site. The A-site occupancy is calculated as 0.51 based on chemical data, but only 0.48 based on X-ray diffraction results. Minerals with the former values would be classified as richterite and those with the latter as winchite.

INTRODUCTION

National attention focused on the small town of Libby, Montana in November 1999 when a newspaper article in the Seattle Post-Intelligencer chronicled asbestos-related diseases found in local miners, with the asbestos contaminant suggested to be the amphibole mineral tremolite. Within days, the United States Environmental Protection Agency arrived in Libby and began an investigation and remediation effort; the area is now a Superfund site. These recent actions are connected to the now-closed vermiculite mine located near Libby. The mine operated from the 1920s until 1990 and had the world's largest vermiculite production; however, the vermiculite ore contained several percent amphibole, both asbestiform and non-asbestiform varieties (Gunter et al. 2001). In the mid 1980s, two independent research groups, one funded by W.R. Grace, owners of the mine (McDonald et al. 1986a, 1986b, 1988), and another funded by the National Institute for Occupational Safety and Health (Amandus and Wheeler 1987; Amandus et al. 1987a, 1987b) performed health studies and found elevated mortality rates from asbestosis, mesothelioma, and lung cancer in the former miners.

The vermiculite mine was located in a Cretaceous-age ultramafic igneous body composed of a series of ring dikes with a post-mining, near-circular exposure of about 3 km in diameter. The ultramafic complex is adjacent to and associated with a syenite body that intruded metamorphic rocks of Precambrian age. The intrusion is roughly concentric and consists of a biotitite core surrounded by biotite pyroxenite, which is in turn surrounded by a magnetite pyroxenite. (see Boettcher 1967 for a detailed discussion of the geology and a geologic map.) The biotite in the biotite pyroxenite was altered to vermiculite by low-temperature weathering, whereas the pyroxenes were altered to amphiboles under higher-temperature hydrothermal processes (Boettcher 1966). Most of the mining was in the biotite pyroxenite. After the vermiculite ore was mined and enriched, it was expanded by rapid heating to form the commercial product Zonolite, which was used in many consumer products such as absorbents, fireproofing materials, industrial fillers, packaging material, and soil amendments. Another of the major uses of Zonolite was in attic insulation. Recently, W.R. Grace estimated that this product is in 15 million homes in the United States. Unfortunately, Zonolite may contain traces of amphiboles and amphibole-asbestos up to 2.8 wt% (USEPA 2000). There is an ongoing debate about the possible health effects on the residents of these homes (USEPA 2001). For a more detailed overview of the mining, geology, mineralogy, and health studies, see Bandli (2002) and references therein.

In a previous study, Wylie and Verkouteren (2000) performed chemical analyses of two amphibole samples from the former mine site. They identified the samples as winchite and

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not, as reported numerous times, tremolite or actinolite (e.g., Amandus and Wheeler 1987; Amandus et al. 1987a, b; MacDonald et al. 1986a, 1986b, 1988; USEPA 2000). However, Wylie and Verkouteren (2000) did not report $Fe^{3+}/\Sigma Fe$ values or F analyses of their two samples. Nor had they personally collected either of the samples. The location of their sample no. 1 was not known, and the location of recently collected sample no. 2 was reported simply as "the mine dump." Not only were there several mine dumps at the former mine site, but the samples in the mine dump may have been from overburden and not from the mining area. In the present study, we analyzed both of their samples for $Fe^{3+}/\Sigma Fe$ and performed a crystal structure refinement of a single crystal of their sample no. 2. We also performed chemical analyses and determined $Fe^{3+}/\Sigma Fe$ values for three samples we collected in the biotite pyroxene zone of the mine.

Asbestos classification and amphibole species names

Regulatory agencies classify certain species of amphibole as asbestos when they occur in the asbestiform habit. These regulated species are riebeckite, cummingtonite-grunerite, anthophyllite, and actinolite-tremolite (USEPA 2000). Tremolite, for example, occurs in both a regulated asbestiform habit and non-regulated, non-asbestiform habit. It is a continuing challenge to appropriately apply the definition of asbestos, applicable to populations of fibers, to the counting of individual particles in samples. Only samples of the above-listed species of amphiboles are regulated as "asbestos." Other amphibole species, however, occur in asbestiform varieties, such as winchite (Wylie and Huggins 1980 and Table 1) and richterite (vein sample, Table 1). The amphibole "asbestos" occurring at Libby has proven to be very harmful (McDonald et al. 1986a, 1986b, 1988; Amandus and Wheeler 1987; Amandus et al. 1987a, 1987b), and it is now apparent that much of the amphibole at Libby is non-regulated winchite and richterite.

Amphibole nomenclature (i.e., the naming of species) is complex because of the variations in chemistry and the many substitutions that occur in this mineral group. Leake et al. (1997) divided amphiboles into four groups based on B-site occupancy, given the general formula $AB_2C_5T_8O_{22}(OH)_2$, as follows: (1) the magnesium–iron–manganese–lithium group, where $(Ca + Na)_B < 1.0$ and $(Mg + Fe + Mn + Li)_B \geq 1.0$; (2) the calcic group, where $(Ca + Na)_B \geq 1.0$ and $Na_B \leq 0.5$; (3) the sodic-calcic group, where $(Ca + Na)_B \geq 1.0$ and $0.5 < Na_B < 1.5$; and (4) the sodic group, where $Na_B \geq 1.5$. Approximately eighty species names were then classified in each of the four groups based on Si content, $Mg / (Mg + Fe^{2+})$ ratio, and more detailed subdivisions of both the A- and B-site occupancies. In the general formula used by Leake et al. (1997), "C" refers to the sum of the contents of the M1, M2, and M3 octahedral sites and B refers to the larger M4 octahedral site. Both winchite and richterite are sodic-calcic amphiboles [i.e., $(Ca + Na)_B \geq 1.0$ and $0.5 < Na_B < 1.5$], whereas tremolite is a calcic amphibole [i.e., $(Ca + Na)_B \geq 1.0$ and $Na_B \leq 0.5$]. The important point here is that a slight change in the B-site occupancy places these species into different groups. Winchite and richterite are distinguished from each other based on their A-site occupancy, with winchite having $(Na + K)_A < 0.5$ and richterite $(Na + K)_A \geq 0.5$.

Sample selection and data collection

Five samples were selected for this study, and two of these, WV no. 1 and WV no. 2, are the same specimens examined by Wylie and Verkouteren (2000). WV no. 1 had been collected "ten-years earlier" from an unknown location at the mine site, and WV no. 2 was recently collected from a "mine dump." Their locations and geological occurrences are unknown. Bulk samples from their study were used to determine $Fe^{3+}/\Sigma Fe$ by Mössbauer spectroscopy, and a single crystal from WV no. 2 was selected for structural and electron microprobe (EMPA) analysis. No new EMPA data were collected from WV no. 1.

M.E. Gunter collected three samples called "vein," "outcrop," and "float" in October 1999 from the biotite pyroxenite zone in the center of the former Libby vermiculite mine. These samples were chosen to represent the different modes of occurrence of the amphiboles observed at the mine. The vein sample came from an approximately 2 cm wide vein of cross-fiber amphibole cross-cutting the biotite pyroxenite. The outcrop sample was collected in place, on a former mined-out bench of biotite pyroxenite; the sample showed an intergrowth of pyroxenes and amphiboles, in which the amphiboles were apparent alteration products of the pyroxenes. The float sample, an approximately 2–3 kg boulder consisting almost entirely of amphibole, was collected in the same area. For all three of these samples, Mössbauer spectroscopy was performed on bulk samples to determine $Fe^{3+}/\Sigma Fe$, and EMPA was done on single particles to obtain a complete chemical analysis.

EXPERIMENTAL METHODS AND RESULTS

Electron microprobe analysis (EMPA)

Several grains of the three Libby amphibole samples (vein, outcrop, and float) were dispersed in epoxy on three separate standard petrographic slides. The samples were an approximately 50–50 mixture of amphibole fibers and fragments (Gunter et al. 2001). Because of the friable nature of the particles and their small size (minimum width approximately 1 µm) much work was required to obtain a suitable polish. A similar preparation method was used for a single crystal from sample WV no. 2* (the "*"denotes this as the crystal used in the structure analysis). The amphiboles were analyzed in the GeoAnalytical Laboratory, Washington State University, using a Cameca Camebax electron microprobe employing wavelength dispersive spectrometry, acceleration voltages of 20 kV (for WV no. 2* and the vein sample) and 15 kV (for the other samples), a beam current of 12 nA, and a beam diameter of 2 µm. The lower accelerating voltage was used for most analyses because of the small grain sizes. A Phi(Rho-Z) absorption correction and conventional fluorescence and atomic number corrections were applied to all data.

Table 1 lists compositions of the samples used in this study. The data in the first two columns in Table 1 are taken from Wylie and Verkouteren (2000). Column three shows the composition of WV no. 2* and represents an average of 25 analyses collected from the single crystal. Listings for the vein, outcrop, and float samples represent an average of 16 analyses from eight separate crystals, one analysis of each of nine crystals, and one analysis of each of 16 crystals, respectively. The compositional variability within the single crystals in the vein sample is similar to the variability among the individual samples, so we chose to perform only one analysis per crystal. We noted no chemical variability as a function of morphology (i.e., fibers vs. fragments). Also listed in Table 1 are the $Fe^{3+}/\Sigma Fe$ ratios (to be discussed later). Chemical formulas were calculated based on 23 (O) for WV no. 1 and WV no. 2 and 24 (O, OH, F, Cl) for WV no. 2* and the three Libby samples we collected. Site assignments were made following the recommendations of Leake et al. (1997).

Mössbauer spectroscopy

Mössbauer spectroscopy studies of amphiboles date back to the original work by Bancroft and coworkers (Bancroft et al. 1967a, 1967b; Bancroft and

TABLE 1. Electron microprobe analyses for amphiboles in this study and the study by Wylie and Verkouteren (2000)

	WV no. 1	WV no. 2	WV no. 2*	Vein	Outcrop	Float
SiO_2	56.6(4)	56.4(2)	57.46(38)	57.10(27)	57.54(41)	57.45(64)
Al_2O_3	0.5(1)	0.4(1)	0.32(4)	0.14(3)	0.13(3)	0.19(10)
TiO_2	nd	nd	0.10(2)	0.11(8)	0.04(3)	0.12(10)
FeO†	2.54	1.49	1.63(5)	2.29(21)	1.97(30)	1.51(20)
Fe_2O_3	3.85	3.01	3.29(10)	4.63(43)	4.93(75)	4.40(60)
MgO	20.2(5)	21.0(4)	21.43(23)	20.19(38)	20.10(78)	20.83(48)
MnO	0.1(0)	0.3(3)	0.32(8)	0.47(6)	0.16(4)	0.09(3)
CaO	8.3(10)	8.8(2)	7.51(17)	6.04(70)	7.63(1.63)	8.07(84)
Na_2O	3.2(8)	3.4(2)	4.35(21)	4.93(49)	3.84(1.04)	3.67(43)
K_2O	0.7(1)	0.8(2)	1.08(5)	1.25(24)	0.93(26)	0.82(11)
H_2O (diff)	nd	nd	1.77(5)	1.82(14)	1.93(10)	1.99(8)
F	nd	nd	0.84(12)	0.68(28)	0.48(19)	0.34(14)
Total‡			99.76(45)	99.37(52)	99.47(53)	99.34(54)
$Fe^{3+}/\Sigma Fe$	57.7	64.5	64.5	64.5	69.3	72.4
FeO_{EMPA}	6.0(6)	4.2(4)	4.59(13)	6.46(59)	6.40(97)	5.47(74)
No. analyses	6	3	25	16	9	16
pfus	for 23O	for 23O	for 24O	for 24O	for 24O	for 24O
Si	7.98	7.95	7.97(3)	7.99(2)	8.01(4)	7.98(4)
Al	0.08	0.07	0.05(1)	0.02(0)	0.02(10)	0.03(2)
Ti	nd	nd	0.01(0)	0.01(1)	0.00(0)	0.01(1)
Fe^{2+}	0.30	0.18	0.19(1)	0.27(2)	0.23(4)	0.18(2)
Fe^{3+}	0.41	0.32	0.34(1)	0.49(4)	0.52(8)	0.46(6)
Mg	4.24	4.43	4.43(4)	4.21(8)	4.17(15)	4.32(9)
Mn	0.01	0.04	0.04(1)	0.06(1)	0.02(1)	0.01(0)
Ca	1.25	1.34	1.12(2)	0.91(10)	1.14(24)	1.20(13)
Na	0.87	0.93	1.17(6)	1.34(14)	1.04(29)	0.99(12)
K	0.13	0.14	0.19(1)	0.22(4)	0.17(5)	0.15(2)
H	nd	nd	1.63(5)	1.70(12)	1.79(9)	1.85(6)
F	nd	nd	0.37(5)	0.30(12)	0.21(9)	0.15(6)
Site occupancies						
T-Si	7.98	7.95	7.97	7.99	8.01	7.98
T-Al	0.02	0.05	0.03	0.01	–	0.02
T-Ti	–	–	–	–	–	–
Sum T	8.00	8.00	8.00	8.00	8.01	8.00
C-Al	0.06	0.02	0.02	0.01	0.02	0.01
C-Ti	–	–	0.01	0.01	0.00	0.01
$C-Fe^{2+}$	0.29	0.18	0.19	0.27	0.23	0.18
$C-Fe^{3+}$	0.41	0.32	0.34	0.49	0.52	0.46
C-Mg	4.24	4.43	4.43	4.21	4.17	4.32
C-Mn	–	0.04	0.01	0.01	0.02	0.01
Sum C	5.00	4.99	5.00	5.00	4.96	4.99
$B-Fe^{2+}$	0.01	–	–	–	–	
B-Mn	0.01	–	0.03	0.05	–	–
B-Ca	1.25	1.34	1.12	0.91	1.14	1.20
B-Na	0.73	0.66	0.85	1.04	0.86	0.60
Sum B	2.00	2.00	2.00	2.00	2.00	2.00
A-Na	0.14	0.27	0.32	0.30	0.18	0.19
A-K	0.13	0.14	0.19	0.22	0.17	0.15
Sum A	0.27	0.41	0.51	0.52	0.35	0.34

Note: All EMPA data are from this study, except values in columns 1 and 2, which are from Wylie and Verkouteren (2000).
* WV no. 2 remeasured in this study.
† FeO and Fe_2O_3 are recalculated from the EMPA FeO and the Mössbauer $Fe^{3+}/\Sigma Fe$. Cl was included in EMPA analyses on our samples but was below 0.01 pfus.
‡ Totals corrected for F.

Burns 1969; Bancroft and Brown 1975). Spectroscopists now follow the site assignments (Table 2) proposed by Goldman (1979). However, only limited work has been done on samples from the sodic-calcic subgroup of the amphiboles. Virgo (1972) reported the first spectra of richterite, followed by the work of Litvin et al. (1973) on taramite. Luys et al. (1983) reported spectra of "amosite," "crocidolite," and anthophyllite asbestos. Ghose et al. (1986) reported Mössbauer spectra of Mn-rich winchite, as did Nysten and Skogby (1994). Most recently, Schmidbauer et al. (2000) gave Mössbauer data for three calcic amphiboles, Sokolova et al. (2000) reported spectra of an unusual strontian potassic-richterite, and Sokolova et al. (2001) gave data for ferrian winchite similar to the one studied here. However, no one has taken advantage of recent advances in fitting Mössbauer spectra. Because there is no analytical solution for the transmission integral represented by a Mössbauer spectrum (Vanderberghe et al. 1994), various methods for simplifying the problem of fitting the spectra were proposed. These include fitting: (1) pure Lorentzian line shapes (as used in the studies just mentioned); (2) a Gaussian distribution of Lorentzian line shapes, known as a Voigt line shape (Voigt 1912); and (3) quadrupole splitting or hyperfine field distributions (Ping et al. 1991). To date, the first of these procedures is the only one to be commonly used worldwide because commercial software for the other two approaches has not been available until very recently.

The approach of fitting quadrupole splitting distributions (QSD) has been shown to be superior to the Lorentzian-based approach in spectra in which there are poorly resolved quadrupole pairs, as is the case in mica (and probably amphibole) spectra. The QSD approach works best in samples where the Fe atoms

TABLE 2. Quadrupole splittings for sodic and calcic amphiboles* (Adapted and updated from Goldman 1979)

Species	M1	M2	M3	M4	Citation
Tremolite-actinolite Fe^{2+}	2.60–2.90	1.70–1.90	2.20–2.60	n.a.	Burns and Greaves (1971)
Hornblende Fe^{2+}	2.79–2.84	2.01–2.09	2.59–2.70	1.70	Bancroft and Brown (1975) Goodman and Wilson (1976)
Magnesio-hastingsite Fe^{2+}	2.70	2.00	2.70	n.a.	Semet (1973)
Sodic amphiboles Fe^{2+}	2.80	2.00	2.40	n.a.	Bancroft and Burns (1969) Ernst and Wai (1970)
Calcic amphiboles Fe^{2+}	2.80 with M3	2.20	2.80 with M1	1.80	Goldman (1979)
Calcic amphiboles Fe^{2+}	2.61–2.79	2.21–2.50		1.80–1.91	Schmidbauer et al. (2000)
Sodic amphiboles Fe^{3+}		0.42–0.50			Ernst and Wai (1970)
Sr potassirichterite Fe^{3+}		0.67			Sokolova et al. (2000)
Ferrian winchite Fe^{3+}		0.48			Sokolova et al. (2001)

Note: n.a. = not analyzed or fitted.
*All quadrupole splittings are from room-temperature spectra and are presented in mm/s. Isomer shifts are not tabulated because they are constant, over a range from 1.10–1.15 mm/s for Fe^{2+} and 0.35–0.48 for Fe^{3+}.

are not surrounded by a perfectly homogeneous array of neighbors and next-nearest neighbors. Effectively, the QSD models the local distortions and atomic disorder surrounding the Fe atoms, rather than simply reflecting the ideal point symmetries of the relevant sites (Rancourt 1994a). In a series of papers, Rancourt and coworkers (Rancourt 1994a, 1994b; Rancourt et al. 1994) convincingly demonstrated that the QSD method performs better than the Lorentzian technique. Fits with Lorentzian doublets tend to overestimate the spectral backgrounds, put large wings or tails on the main absorption peaks, give unphysically large linewidths (Rancourt 1994a), and underestimate $Fe^{3+}/\Sigma Fe$ ratios by 1–2%. Thus, for comparison, we have chosen to model our Mössbauer spectra with the three different fitting techniques discussed above.

Samples were prepared for Mössbauer analysis by shredding them with a tweezer and spatula followed by grinding in a mortar and pestle under acetone to avoid oxidation. Approximately 10 mg of each sample, close to the thin absorber thickness as calculated by the method of Long et al. (1983), were then mixed with sugar and acetone and placed in the spectrometer sample holder, which is a plexiglas ring 3/8" in diameter. Although these precautions were undertaken to avoid the effects of preferred orientation, they were probably unnecessary because the crystals were all elongated, approximately equal mixture of fragments and fibers (Gunter et al. 2001). Spectra were acquired using a WEB Research Co. Mössbauer spectrometer in the Mineral Spectroscopy Laboratory at Mount Holyoke College. The instrument is equipped with a Janis Research Co. Model 850 closed-cycle He refrigerator capable of reaching temperatures from 12 to 700 K. Data were analyzed using the software package WMOSS by WEB Research Co., which has the capability to use Lorentzian or Voigt doublets or quadrupole splitting distributions (QSD).

Mössbauer spectra of all the samples are similar (Fig. 1). Results are given in Table 3 and include data from fits using Lorentzian, Voigt, and quadrupole splitting distribution models; a QSD fit is shown in Figure 2. At room temperature, each spectrum is composed of one (for Lorentzian and Voigt) or two (for QSD) $^{M}Fe^{3+}$ doublets/components and two $^{M}Fe^{2+}$ doublets/components. The two $^{M}Fe^{3+}$ components have similar isomer shifts (δ) of 1.12 mm/s but dramatically different values of quadrupole splitting (Δ =1.85 and 2.8 mm/s). Traditionally, these doublets have been assigned to $^{[M4]}Fe^{2+}$ and $^{[M1,M2,M3]}Fe^{2+}$, respectively (cf., Table 2), although some workers (Burns and Greaves 1971) have suggested that the lowest Δ doublet might be assigned to $^{M2}Fe^{2+}$.

One $^{M}Fe^{3+}$ feature, a sharp doublet with δ^{*} = 0.35 mm/s, is typical of octahedral Fe^{3+}. The second $^{M}Fe^{3+}$ component, which is present only in the QSD fits, is a broad feature with a similar isomer shift but very broad full widths at half maximum of the Gaussian. Based on these room-temperature spectra, it appeared that the latter Fe^{3+} component is a contribution from some impurity in

the sample that was broadened by the onset of ferromagnetism (i.e., splitting into a sextet rather than a doublet). Because the majority of silicates undergo this transition at <100 K, this broadened feature strongly suggested the presence of an oxide phase as an impurity and made it clear that low-temperature spectra would be needed to accurately interpret the Mössbauer data from these samples. For this reason, low temperature spectra of the outcrop sample were acquired at 100 K and 12 K; the latter spectrum is shown in Figure 3.

Structure refinement

The X-ray diffraction data for WV no. 2* was collected with a Bruker/ Siemens 3-circle platform SMART diffractometer (χ-axis fixed at 54.74°) at the University of Idaho. The frame data were acquired with the SMART software (SMART 1998) at 303(2) K using MoKα radiation (λ = 0.71073 Å) from a normal-focus tube (see Table 4). Unit-cell constants were determined from 20

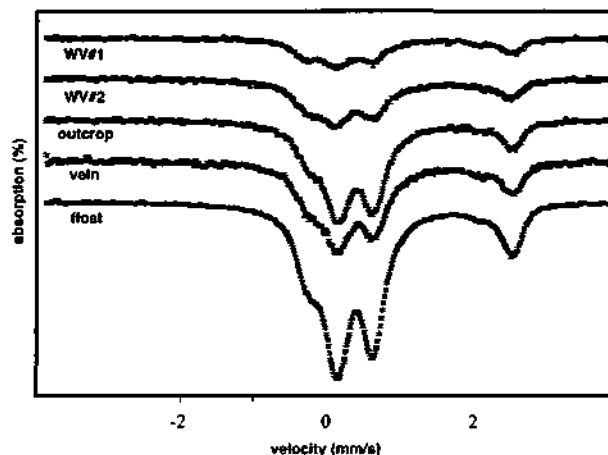
FIGURE 1. Room-temperature Mössbauer spectra of Libby amphiboles. Differences in absorption are due to variable Fe contents and sample thicknesses used; not enough sample was available to allow use of a consistent thickness.

TABLE 3. Results of Mössbauer analysis

Sample	Lineshape	$\chi 2$	Δ_0	σ_D	δ_0	Area	Δ_0	σ_D	δ_0	Area	Δ_0	σ_D	δ_0	Area	Δ_0	σ_D	δ_0	Area	Fe^{3+}_{raw}	Fe^{3+}_{cor}
				Fe^{3+}				Fe^{3+}				$^{(M2)}Fe^{2+}$ (M2)				$^{(M1+M3)}Fe^{2+}$				
WV	Lorentzian	0.56	0.53		0.37	61.5					1.84		1.15	7.6	2.83		1.13	33.6	59.9	55.0
no.1	Voigt	0.81	0.56		0.36	53.8					1.86		1.13	8.8	2.86		1.11	28.7	58.9	54.0
	QSD	0.55	0.51	0.47	0.38	29.2	0.53	2.66	0.35	30.8	1.90	0.00	1.13	7.0	2.86	0.53	1.13	29.1	62.4	57.7
WV	Lorentzian	1.49	0.58		0.37	59.3					1.15		0.77	12.2	2.80		1.07	32.0	57.3	52.4
no.2	Voigt	1.93	0.60		0.36	63.0					1.75		1.10	9.1	2.84		1.09	27.2	63.4	58.7
	QSD	0.60	0.50	0.50	0.40	31.1	0.54	3.07	0.34	44.4	2.11	0.87	1.04	10.8	2.78	0.51	1.15	23.2	68.9	64.5
Vein	Lorentzian	0.53	0.53		0.37	74.4					1.86		1.12	7.1	2.79		1.13	27.0	68.6	64.1
	Voigt	1.18	0.56		0.37	65.1					1.84		1.10	8.1	2.84		1.10	23.2	67.5	63.0
	QSD	0.42	0.49	0.51	0.40	37.1	0.38	2.88	0.33	35.4	1.93	0.62	1.10	10.0	2.85	0.51	1.15	22.7	68.9	64.5
Outcrop	Lorentzian	6.80	0.51		0.38	75.2					1.84		1.09	5.8	2.79		1.13	25.4	70.7	66.4
	Voigt	20.90	0.53		0.37	67.3					1.81		1.09	6.2	2.82		1.11	22.8	69.9	65.5
	QSD	1.58	0.49	0.40	0.39	42.0	0.37	2.57	0.29	32.7	1.95	0.73	1.09	7.0	2.77	0.46	1.14	20.2	73.3	69.3
Float	Lorentzian	0.74	0.51		0.38	79.0					1.82		1.13	3.4	2.78		1.13	22.6	75.2	71.4
	Voigt	2.39	0.53		0.37	69.8					1.82		1.10	5.2	2.83		1.10	19.7	73.7	69.6
	QSD	0.51	0.50	0.45	0.38	44.7	0.28	2.88	0.33	33.0	1.85	0.60	0.69	6.7	2.77	0.44	1.19	17.6	76.2	72.4

Notes: Values of δ_i are 0.02 or less in all cases for fits using quadrupole splitting distributions. Γ is constrained to be equal to 0.20 mm/s, and h+/h− is constrained to be equal to 1. Symbols follow Rancourt and Ping (1991). Fe^{3+}_{raw} is the calculated peak area assigned to Fe^{3+}. Fe^{3+}_{cor} is the "true" corrected Fe^{3+} content based on a value of 1.22 for the recoil-free fraction correction in amphibole (cf., Dyar et al. 1993 for more information).

TABLE 4. Crystal structure collection methods and results

Temperature	303(2) K
Wavelength	0.71073 Å
Space group	*C2/m*
Unit cell dimensions	$a = 9.8787(18)$ Å
	$b = 18.024(3)$ Å
	$c = 5.2875(10)$ Å
	$\beta = 104.377(3)°$
	Volume = 912.0(3) Å³
Density (calculated)	3.013 Mg/m³
Absorption coefficient	1.691 mm⁻¹
$F(000)$	823
Crystal size	0.39 × 0.14 × 0.11 mm³
Diffractometer	Siemens SMART 1K
Theta range for data collection	2.41 to 24.99°.
Index ranges	$-9 \le h \le 11, -21 \le k \le 18, -6 \le l \le 6$
Reflections collected	2763
Independent reflections	834 (R_{int} = 0.0207)
Completeness to theta = 24.99°	99.4%
Absorption correction	Empirical*
Solution method	XS, Bruker SHELXTL v. 5.10
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0335$, wR_2 = 0.0994
R indices (all data)	$R_1 = 0.0419$, wR_2 = 0.1043
Largest diff. peak and hole	0.699 and −0.739 e.Å⁻³

Note: $R_1 = \Sigma |F_o| - |F_c|/\Sigma |F_o|$; w$R_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
* SADABS (1999).

10 s frames. A complete hemisphere of data was scanned on omega (0.3° per scan) with a run time of 30 s per frame at the detector resolution of 512 × 512 pixels. A total of 1421 frames were collected in four sets, and a final set of 100 frames identical to the first 100 frames was also collected to determine crystal decay. The frames were then processed using the SAINTPlus software (SAINTPlus 1999) to give the raw data corrected for Lp/decay. The crystal used for the diffraction study showed no decomposition during data collection. The absorption correction was performed using the SADABS program (SADABS 1999). The structures were solved by direct method using SHELXS and refined by least squares method on F^2, using SHELXL; both programs are a part of SHELXTL v. 5.10 (SHELXTL 1998).

All non-hydrogen atoms were refined anisotropically. Site occupancies were initially assigned from diffraction data and then modeled until thermal parameters were approximately equal. Fractional positions and thermal parameters for the shared site atoms were also made equal. The A site (K, Na) is not completely filled (site occupancy factor of 0.48) and the low electron density and anisotropic refinement led to a prolate thermal displacement ellipsoid for this site. Ti was not included in the refinement because of its low concentration

(0.01 apfu). The H atom (Table 5) was located on the difference map and refined with an occupancy equal to O3, which is a shared site atom. Atomic coordinates and temperature factors are given in Table 5, site occupancy data are given in Table 6, and selected bond lengths and the observed and calculated mean bond lengths for M1, M2, M3, and A are given in Table 7. The mean bond lengths are calculated based on the equation given in Hawthorne (1983). There is good agreement between the observed and calculated values, which helps validate our site assignments.

DISCUSSION

Low-temperature Mössbauer spectra

The low-temperature spectra proved to be the key to understanding the valence state of iron in these samples. A spectrum of the outcrop sample is shown in Figure 3. No sharp sextet is visible in this expanded-scale spectrum, indicating an absence of ferromagnetism. Thus, the broad Fe^{3+} component observed in the Libby amphibole spectra cannot be assigned to an impurity but must be contained within the amphibole crystal structure. This feature is consistent with the site occupancies calculated with Lorentzian and Voigt line shapes. For the "final" chemical compositions in Table 1, we used the area of the two Fe^{3+} components from the QSD fits, adjusted for the recoil-free fraction. Two possible explanations could explain the broad component observed in the QSD fits: (1) there is a distribution in crystal size, with some grains less than 1–10 μm wide (Gunter et al. 2001), or (2) the observed feature corresponds to isolated magnetic states for Fe^{3+}.

Effect of curve-fitting the line-shape for Mössbauer spectra

Because one of the goals of this project was to determine the Fe^{3+} contents of the Libby amphiboles, differences in $\%Fe^{3+}$ content that might result from fitting procedures were important. The far right-hand column of Table 3 shows the calculated Fe^{3+} content of the samples. The maximum variation due to the fitting model was observed for sample WV no. 2, which had a spread of 12.1% (absolute) in Fe^{3+} content. For all the
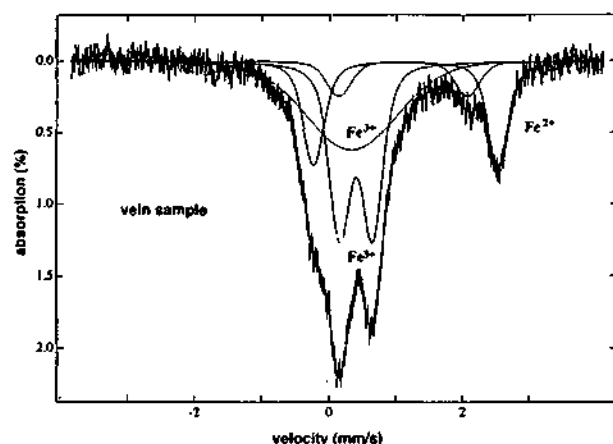
FIGURE 2. Mössbauer spectrum (dark curves showing noise) of the vein sample fitted using the quadrupole splitting distribution model (components shown as thin, smooth lines).
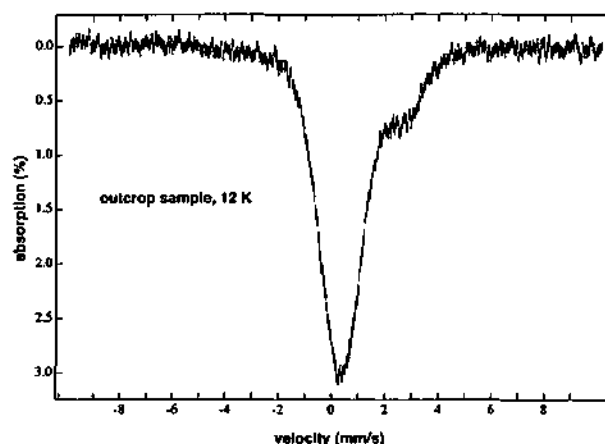
FIGURE 3. Low-temperature Mössbauer spectrum of the outcrop sample. Note the lack of features in the region from -10 to -3 and >4 mm/s, which indicates the absence of ferromagnetic species in this sample.

TABLE 5. Atomic coordinates and equivalent isotropic displacement parameters for WV no. 2*

Site	x/a	y/b	z/c	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
T1	0.2791(1)	0.0848(1)	0.2960(2)	0.011(1)	0.015(1)	0.011(1)	0.008(1)	-0.001(1)	0.005(1)	0.000(1)
T2	0.2872(1)	0.1714(1)	0.8031(2)	0.011(1)	0.015(1)	0.012(1)	0.007(1)	0.000(1)	0.004(1)	-0.001(1)
M1	0.	0.0886(1)	0.5	0.009(1)	0.013(1)	0.009(1)	0.005(1)	0.	0.003(1)	0.
M2	0.	0.1796(1)	0.	0.010(1)	0.012(1)	0.011(1)	0.007(1)	0.	0.004(1)	0.
M3	0.	0.	0.	0.020(1)	0.026(1)	0.020(1)	0.016(1)	0.	0.007(1)	0.
M4	0.	0.2772(1)	0.5	0.018(1)	0.024(1)	0.016(1)	0.018(1)	0.	0.012(1)	0.
A	0.	0.5	0.	0.105(4)	0.127(8)	0.058(5)	0.188(11)	0.	0.147(8)	0.
O1	0.1113(2)	0.0865(1)	0.2166(4)	0.013(1)	0.017(1)	0.013(1)	0.008(1)	-0.001(1)	0.004(1)	-0.001(1)
O2	0.1186(2)	0.1702(1)	0.7269(4)	0.014(1)	0.017(1)	0.015(1)	0.011(1)	-0.001(1)	0.005(1)	-0.001(1)
O3	0.1081(3)	0.	0.7138(6)	0.014(1)	0.018(2)	0.016(2)	0.010(2)	0.	0.006(1)	0.
O4	0.3634(2)	0.2487(1)	0.7956(4)	0.015(1)	0.020(1)	0.015(1)	0.009(1)	-0.001(1)	0.005(1)	-0.004(1)
O5	0.3459(2)	0.1315(1)	0.0922(4)	0.015(1)	0.018(1)	0.018(1)	0.010(1)	0.004(1)	0.005(1)	0.000(1)
O6	0.3419(2)	0.1182(1)	0.5877(4)	0.014(1)	0.017(1)	0.015(1)	0.011(1)	-0.002(1)	0.004(1)	-0.001(1)
O7	0.3364(3)	0.	0.2935(6)	0.016(1)	0.013(2)	0.016(2)	0.016(2)	0.	0.004(1)	0.
H	0.2148	0.	0.7750	0.030(20)	nd	nd	nd	nd	nd	nd

Note: U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, and anisotropic displacement parameters, where the anisotropic displacement factor exponent takes the form: $-2\pi2[h2 \ a*2 U_{11} + ... + 2 \ h \ k \ a* \ b* \ U_{12}]$.

TABLE 6. Cation site occupancies determined by X-ray diffraction (XRD), Mössbauer spectroscopy (Möss), and EMPA for WV no. 2*

	Si	Al	Mg	Fe Fe^{3+} / Fe^{2+}*	Mn	Ca	Na	K	Site sum
T	7.96	0.04							8.00
M1		0.02	1.98						2.00
M2			1.64	0.36 0.34 / 0.06					2.00
M3			0.84	0.16 0.00 / 0.13					1.00
M4					0.04	1.12	0.84		2.00
A							0.28	0.20	0.48
Sums from XRD & Möss		0.06	4.46	0.52 0.34 / 0.19	0.04	1.12	1.12	0.20	
Sums from EMPA	7.96	0.06	4.46	0.52 0.34 / 0.19	0.04	1.12	1.17	0.19	

* Fe^{3+} / Fe^{2+} site occupancies determined by Mössbauer spectroscopy.

other samples, the spread was less than 3% absolute. This result suggests that, in this suite of samples, the measured Fe^{3+} content is not model-dependent. As predicted by Rancourt (1994a, b) and Rancourt et al. (1994), the QSD model does tend to give slightly higher Fe^{3+} contents than the older models. This result suggests that Mössbauer analyses reported in earlier studies need not be discarded, but should definitely be reported with slightly larger errors than previously reported.

Site occupancies of Fe and other atoms

In this study, two different techniques were used to evaluate the occupancies of the Fe sites: Mössbauer spectroscopy

TABLE 7. Selected bond distances, observed mean bond distances, and calculated mean bond distances for M1, M2, and M3-sites for WV no. 2*

Bonds	Distances (Å)	Bonds	Distances (Å)
T1-O1	1.606(2)		
T1-O5	1.630(2)		
T1-O6	1.627(2)	M3-O1 ×4	2.080(2)
T1-O7	1.631(2)	M3-O3 ×2	2.058(3)
<T1-O>$_{obs}$	1.624	<M3-O>$_{obs}$	2.073
		<M3-O>$_{calc}$	2.068
T2-O2	1.613(3)		
T2-O4	1.589(3)		
T2-O5	1.658(2)	M4-O2 ×2	2.415(3)
T2-O6	1.679(2)	M4-O4 ×2	2.351(2)
<T2-O>$_{obs}$	1.635	M4-O5 ×2	2.836(2)
		M4-O6 ×2	2.564(2)
M1-O1 ×2	2.067(2)	<M4-O>$_{obs}$	2.542
M1-O2 ×2	2.068(2)		
M1-O3 ×2	2.091(2)		
<M1-O>$_{obs}$	2.075		
<M1-O>$_{calc}$	2.076	A-O5 ×4	2.923(2)
		A-O6 ×4	3.167(2)
M2-O1 ×2	2.171(2)	A-O7 ×2	2.503(3)
M2-O2 ×2	2.080(2)	<A-O>$_{obs}$	2.937
M2-O4 ×2	1.983(2)		
<M2-O>$_{obs}$	2.078		
<M2-O>$_{calc}$	2.069		

and single crystal X-ray diffraction, for which we obtained EMPA data from the crystal used for structure analysis. In order to use the Mössbauer effect to determine site occupancies, it is necessary to use the QSD model. Rancourt (1994a) showed the inadequacy of Lorentzian doublets for fitting spectra of naturally occurring mica samples. Rancourt (1994b) further noted that "fitting with Lorentzian doublets can at best give phenomenological characterizations of spectra, whereas QSDs are true physical quantities amenable to theoretical calculations and crystal chemical interpretation." He showed that Mössbauer spectra of 2:1 layer silicates cannot resolve the octahedral Fe^{2+} cis (M2) and trans (M1) sites, and he supported his contention that "interpretations in terms of octahedral Fe^{2+} cis and trans sites are incorrect and cannot be used to even estimate cis/trans site population ratios." Rancourt (1994b) then concluded by strongly stating that "we recommend that spectroscopists now break from this admittedly compelling interpretation (of Lorentzian line shape doublets assigned to cis and trans sites) to consider the QSD."

A similar physical situation exists for the amphibole group minerals, which can be expected to have heterogeneous configurations of next nearest neighbor atoms because they are compositionally so variable and complex. Thus, it is important to consider whether the traditional assignments of amphibole Mössbauer spectra to Fe at specific sites in the structure are robust. Several studies have compared the results of Mössbauer site assignments (calculated using Lorentzian line-shapes) to the results of single-crystal X-ray diffraction (XRD). For example, Evans et al. (2001) showed strong agreement between the Mössbauer data of Seifert (1978) and their own single-crystal XRD results for two-doublet Lorentzian fits to Fe^{2+} doublets assigned to M4 and M1-3. A comparison of XRD and Mössbauer data from a suite of cummingtonite samples was carried out by Grant (1995). He suggested that excellent agreement between XRD and Mössbauer site occupancies in amphibole can be obtained if thickness and recoil-free fraction

effects are considered, along with use of Voigt or QSD lineshapes.

There is consistency between our Mössbauer and XRD results. As shown in Table 3, 64.5% of the total Fe is Fe^{3+}, or 0.34 apfu, and 35.5%, or 0.19 apfu, is Fe^{2+} (Table 1, WV no. 2*). The Fe^{2+} doublet with the lowest quadrupole splitting is assigned to $^{M7}Fe^{2+}$, following the convention of Burns and Greaves (1971), while the other Fe^{2+} doublet represents an unresolvable combination of $^{M1+M3}Fe^{2+}$. Because the site refinement shows only Mg and Al at the M1 site, we conclude that this doublet here represents only $^{M3}Fe^{2+}$. Thus, of the Fe^{2+}, 31.8% or 0.06 apfu is at M2, and 68.2% or 0.13 apfu is at M3, compared to 0.16 apfu Fe by XRD (Table 6). Overall, there is excellent agreement between the two techniques, similar to what has been observed in previous studies. Therefore, for amphibole group minerals (unlike the situation for micas) it is probably still appropriate to use Mössbauer fits to assign site occupancies for Fe.

All the cation assignments, including Fe, are listed in Table 6. In addition to the excellent agreement between the Mössbauer and XRD results for Fe, there is also excellent agreement between the XRD data and the EMPA data as revealed by the "sums" row in Table 6. The site assignment method from Leake et al. (1997) cannot discriminate between M1, M2, and M3 when treating all of them as "C" in the general formula A B_2 C_5 T_8 O_{22} $(O,OH,F,Cl)_2$, but when the contents of "C" (Table 1), as assigned according to the method of Leake et al. (1997), are compared to the summed contents of M1, M2, and M3 in Table 6, they are also in excellent agreement. One reason for the agreement between XRD and EMPA results is that both sets of data were collected from the same single crystal, which is often not the case. Frequently one will assume that chemical results will be the same for crystals "out-of-the-same-bottle." As shown in Table 1, this is not the case; there is a significant difference in composition between WV no. 2 and WV no. 2*. Also, as stated above, significantly different compositions were found in the suite of three samples from Libby. Significant variation between crystals from the same samples was also observed. For example, for the 16 different crystals analyzed for the float sample, the apfu values ranged from 1.03 to 1.42 for Ca and 0.78 to 1.18 for Na. While some of this is experimental error in the EMPA data, some of the variation could represent compositional differences.

Libby amphiboles: chemical formulas, species names, and implications for asbestos classification

To date there have been six published chemical analyses of single crystals of amphibole from the former vermiculite mine near Libby (summarized in Table 1). Based on the site assignments in Table 1 and the classification scheme of Leake et al. (1997), all of these samples belong to the sodic-calcic group of amphiboles. At the species level, two of these samples are classified as richterite (A-site occupancy ≥0.5) and four as winchite (A-site occupancy <0.5). Interestingly, WV no. 2 and WV no. 2* might be classified as winchite and richterite, respectively, based on compositional determinations made by two different research groups. Our chemical analysis was not obtained from the same single crystal as that of Wylie and Verkouteren (2000),

but rather from a crystal from the same bulk sample. Of course, some chemical variation within these natural samples might be expected. Moreover, of the 25 analyses of WV no. 2*, which were averaged in Table 1 to arrive at the final formula, 11 had A-site occupancies less than 0.5. This would define the sample as a winchite. Thus, this sample resides compositionally at the boundary between these two species. In addition, four bulk-sample analyses of Libby amphiboles have been published to date: a wet chemical analysis by Larsen (1942) showed richterite; three bulk-sample XRF analyses by Gunter et al. (2001) on the same suite of samples used in this study (vein, outcrop, float) all showed winchites. The XRF analysis of bulk samples (Gunter et al. 2001) yielded slightly higher Al and K concentrations and lower Ca and Mg concentrations than the single crystals studied here. This result probably reflects microscopic impurities of sheet silicates in the bulk samples.

Historically, the amphiboles at Libby were called tremolite or actinolite by the majority of workers in the health fields (McDonald et al. 1986a, 1986b; Amandus and Wheeler 1987; Amandus et al. 1987a, 1987b; McDonald et al. 1988; Weill et al. 1990), regulatory agencies (USEPA 2000), and by the media. Our data and those of Wylie and Verkouteren (2000) suggest instead that these amphiboles are dominantly winchites and richterites. There is no doubt that it is important for mineralogists and petrologists to set criteria for precise definition of mineral species names, as was done by Leake et al. (1997). Others in the sciences and regulatory fields must use these names to avoid confusion. However, we must realize the limitations to placing a name on a mineral that occurs in a solid solution series. For instance, using winchite and richterite as examples, a winchite with an A-site occupancy of 0.49 would be more similar (i.e., its physical, structural, and chemical properties) to a richterite with an A-site occupancy of 0.50 than it would to a winchite with an A-site occupancy of 0.1, yet the mineral name would be different for the first set and the same for the second.

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SAINTPlus (1999) Version 6.02, Data Reduction and Correction Program, Bruker AXS, Madison, Wisconsin.

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Semet, M. (1973) A crystal-chemical study of synthetic magnesio-hastingite. American Mineralogist, 58, 480–494.

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Sokolova, E.V., Hawthorne, F.C., Gorbatova, V., McCammon, C., and Schneider, J. (2001) Ferrian winchite from the Ilmen Mountains, Southern Urals, Russia and some problems with the current scheme of nomenclature. Canadian Mineralogist, 39, 171–177.

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Vanderberghe, R.E., DeGrave, E., and de Bakker, P.M.A. (1994) On the methodology of the analysis of Mössbauer spectra. Hyperfine Interactions, 83, 29–49.

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Wylie, A.G. and Huggins, C.W. (1980) Characteristics of a potassian winchite-asbestos from the Allamorre talc-district, Texas. Canadian Mineralogist, 18, 101–107.

Wylie, A.G. and Verkouteren, J.R. (2000) Amphibole asbestos from Libby, Montana: Aspects of nomenclature. American Mineralogist, 85, 1540–1542.

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ISO 14966: 2002-11-15
Ambient Air - Determination of Numerical Concentration of Inorganic Fibrous Particles - Scanning Electron Microscopy Method

Abstract

ISO 14966:2002 specifies a method using scanning electron microscopy for determination of the concentration of inorganic fibrous particles in the air. The method specifies the use of gold-coated, capillary-pore, track-etched membrane filters, through which a known volume of air has been drawn. Using energy-dispersive X-ray analysis, the method can discriminate between fibres with compositions consistent with those of the asbestos varieties (e.g. serpentine and amphibole), gypsum and other inorganic fibres. Annex C provides a summary of fibre types which can be measured.

ISO 14966:2002 is applicable to the measurement of the concentrations of inorganic fibrous particles in ambient air. The method is also applicable for determining the numerical concentrations of inorganic fibrous particles in the interior atmospheres of buildings, for example, to determine the concentration of airborne inorganic fibrous particles remaining after the removal of asbestos-containing products.

The range of concentrations for fibres with lengths greater than 5 micrometres, in the range of widths which can be detected under standard measurement conditions, is approximately 3 fibres to 200 fibres per square millimetre of filter area. The air concentrations, in fibres per cubic metre, represented by these values are a function of the volume of air sampled.

NOTE: The ability of the method to detect and classify fibres with widths lower than 0,2 micrometres is limited. If airborne fibres in the atmosphere being sampled are predominantly less than 0,2 micrometres in width, a transmission electron microscopy method such as ISO 10312 can be used to determine the smaller fibres.

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Tabulation of Asbestos-Related Terminology

By Heather Lowers and Greg Meeker

Open-File Report 02-458

2002

U.S. DEPARTMENT OF THE INTERIOR
U.S. GEOLOGICAL SURVEY

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Abstract

The term asbestos has been defined in numerous publications including many State and Federal regulations. The definition of asbestos often varies depending on the source or publication in which it is used. Differences in definitions also exist for the asbestos-related terms acicular, asbestiform, cleavage, cleavage fragment, fiber, fibril, fibrous, and parting. An inexperienced reader of the asbestos literature would have difficulty understanding these differences and grasping many of the subtleties that exist in the literature and regulatory language. Disagreement among workers from the industrial, medical, mineralogical, and regulatory communities regarding these definitions has fueled debate as to their applicability to various morphological structures and chemical compositions that exist in the amphibole and serpentine groups of minerals. This debate has significant public health, economic and legal implications. This report summarizes asbestos-related definitions taken from a variety of academic, industrial, and regulatory sources. This summary is by no means complete but includes the majority of significant definitions currently applied in the discipline.

Table of Contents

Introduction

Ongoing debate in the asbestos community involves a variety of issues, many of which center around nomenclature. A novice to the asbestos literature would have difficulty grasping the significance and subtleties of the many terms used to describe various asbestos-related mineralogical structures. To confound the issue, many of these terms carry different definitions, depending upon the source that is consulted. The purpose of this report is to give the user a consolidated source of the various definitions that have been put forth and are being used. This report is not intended to endorse any particular definition, but rather point out the variations, differences and inconsistencies that exist in the literature.

The tables in this report present a compilation of definitions that have been put forth by mineralogical, industrial, regulatory, and medical workers over the last thirty years for the terms acicular, asbestiform, asbestos, cleavage, cleavage fragments, fiber, fibril, fibrous, and parting. Some definitions of these terms vary from source to source simply because they are intended for specific application in analytical methods. An example is the term *fiber* that may be defined simply by length and width criteria for the purpose of structure counting. Such a definition may not be applicable to a more general use of the term and should not be broadly applied. A person choosing to read an asbestos-related document should be aware of the intent of the definition in the particular publication.

The information in this report is presented in table format. The first column in each table, headed community, will contain one of five categories: interdisciplinary, industrial, medical, mineralogical, or regulatory (including test methods) based on the discipline of the publication in which the term appears. The second heading gives the year the source was published. This allows the reader to see the evolution, if any, of the terms over the years. The third column gives the complete reference for the source indicated. The fourth column includes the definition(s) for each asbestos-related term that is defined in the source. Each table is titled by the term being defined. In all cases, the

definitions of the terms were taken word for word from the source. Comments by the authors of this report are designated by italicized text enclosed by brackets. The same source was searched for all the terms given in this report. If a term was not defined, located, or used in the source, "NA" will appear in the respective column.

This tabulation is by no means complete, but includes the spectrum of definitions given in the academic, industrial, and regulatory literature. It is clear that there is disagreement and perhaps misunderstanding regarding some of the terminology used by workers in various asbestos-related fields. It is hoped that this report will assist the reader in evaluating and understanding the thousands of asbestos-related documents in the literature. For additional perspectives of the evolution of the terms defined in this report, the reader is referred to the following sources:

Langer, A.M., Rohl, A.N., Wolff, M., Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments: Nomenclature and biological properties, *in* Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.

Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.

National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.

Table 1. Acicular

Community	Year	Source	Acicular
Industrial	1975	Winson, R.W., 1975, Asbestos, *in*, Industrial minerals and rocks (nonmetallics other than fuels): New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 379-425.	NA
Industrial	1981	Steel, E. and Wylie, A., 1981, Mineralogical characteristics of asbestos *in* Riordon, P.H. ed, Geology of Asbestos Deposits, Society of Mining Engineers, p. 93-100.	NA
Industrial	1998	Virta, R.L., 2002, Asbestos: U.S. Geological Survey Open File-Report 02-149, 35 p.	NA
Interdisciplinary	1974	Thompson, C.S., 1974, Discussion of the mineralogy of industrial talcs: U.S. Bureau of Mines Information Circular 8639, p. 22-42.	NA
Interdisciplinary	1978	Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.	NA
Interdisciplinary	1979	Chatfield, E.J., 1979, Measurement of asbestos fibres in the workplace and in the general environment *in* Ledoux, R.L., Mineralogical techniques of asbestos determination: Mineralogical Association of Canada Short Course, v. 4, p. 111-157.	NA
Interdisciplinary	1980	Dixon, W.C., 1980, Applications of optical microscopy in analysis of asbestos and quartz, *chap 2 of* Dollberg, D.D. and Werstuyft, A.W., eds., Analytical techniques in occupational health chemistry: Washington, D.C., American Chemical Society, p. 13-41.	NA
Interdisciplinary	1980	Clark, R.L., 1982, MSHA standard method for fiber identification by electron microscopy: National Bureau of Standards Special Publication 619, p. 207-210.	NA

Table 1. Acicular

Community	Year	Source	Acicular
Interdisciplinary	1980	Lee, R.J., Kelly, J.F., and Walker, J.S., 1982, Considerations in the analysis and definition of asbestos using electron microscopy: National Bureau of Standards Special Publication 619, p. 132-137.	NA
Interdisciplinary	1980	Chatfield, E.J. and Lewis, G.M., 1980, Development and application of an analytical technique for measurement of asbestos fibers in vermiculite: Scanning Electron Microscopy, p. 329-340.	NA
Interdisciplinary	1984	National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.	ACICULAR crystals are crystals that are extremely long and thin and have a small diameter. (An acicular crystal is a special type of PRISMATIC crystal. A prismatic crystal has one elongated dimension and two other dimensions that are approximately equal.) As defined by the American Geological Institute (1980), a mineral fragment must be at least three times as long as it is wide to be called acicular. Acicular crystals or fragments are not expected the have the strength, flexibility, or other properties of asbestiform fibers.
Interdisciplinary	1984	Cossette, M., 1984, Defining asbestos particulates for monitoring purposes *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, p. 5-49.	needlelike
Interdisciplinary	1984	Ross, M., Kuntze, R.A., and Clifton, R.A., 1984, A definition for asbestos *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, pp.139-147.	NA
Interdisciplinary	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	Needle-shaped or needlelike. The term is ordinarily applied in mineralogy to straight, greatly elongate, free-standing (individual) crystals bounded laterally, and terminated, by crystal faces. Aggregates of acicular crystals often occur in open, bristly groups. The aspect ratio of acicular crystals is in the same range of those of "fiber" and "fibrous", but the thickness may extend to several millimeters.

Table 1. Acicular

Community	Year	Source	Acicular
Interdisciplinary	1990	Mossman, B.T., Bignon, J., Corn, M., Seaton, A., and Gee, J.B.L., 1990, Asbestos-scientific developments and implications for public policy: Science, v. 247, p. 294-301.	NA
Interdisciplinary	2000	The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2000 by Houghton Mifflin Company.	Having the shape of a needle: *acicular crystals*
Interdisciplinary	2000	Wylie, A.G., 2000, The habit of asbestiform amphiboles: implications for the analysis of bulk samples *in* Beard, M.E. and Rooks, H.L, eds., Advances in environmental measurement methods for asbestos: ASTM Special Technical Publication 1342, p. 53-69.	NA
Interdisciplinary	2001	Beard, M.E., Crankshaw, O.S., Ennis, J.T., and Moore, C.E., 2001, Analysis of crayons for asbestos and other fibrous materials, and recommendations for improved analytical definitions: Research Triangle Park, North Carolina, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, Earth and Mineral Sciences Department, [informal report], 23 p., plus appendices A-H.	NA
Interdisciplinary	2001	Nolan, R.P., Langer, A.M., Ross, M., Wicks, F.J., and Martin, R.F., eds., 2001, The health effects of chrysotile asbestos-contribution of science to risk-management decisions: The Canadian Mineralogist Special Publication 5, 304 p.	NA
Medical	1977	Zielhuis, R.L., 1977, Public health risks of exposure to asbestos: Elmsford, N.Y., Pergamon Press Inc., 143 p.	NA

Table 1. Acicular

Community	Year	Source	Acicular
Medical	1979	Langer, A.M., Rohl, A.N., Wolff, M., and Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments-Nomenclature and biological properties, *in* Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.	NA
Medical	1998	Blake, T., Castranova, V., Schwegler-Berry, D., Baron, P., Deye, G.J., Li, C., and Jones, W., 1998, Effect of fiber length on glass microfiber cytotoxicity: Journal of Toxicology and Environmental Health, v. 54, p. 243-259.	NA
Medical	2001	Ninth Report on Carcinogens, January 2001 http://ehp.niehs.nih.gov/roc/ninth/known/asbestos.pdf	NA
Mineralogical	1914	Dana, E.S., 1914, The system of mineralogy of James Dwight Dana, descriptive mineralogy (6th ed): New York, N.Y., Wiley, p.	NA
Mineralogical	1977	Campbell, W.J., Blake, R.L, Brown, L.L., Cather, E.E., and Sjober, J.J., 1977, Selected silicate minerals and their asbestiform varieties: U.S. Bureau of Mines Information Circular 8751, 56 p.	The shape shown by an extremely slender crystal with small cross-sectional dimensions (a special case of prismatic form). Acicular crystals may be blunt-ended or pointed. The term "needlelike" refers to an acicular crystal with pointed termination at one or both ends.
Mineralogical	1979	Campbell, W.J., Steel, E.B., Virta, R.L., and Eisner, M.H., 1979, Relationship of mineral habit to size characteristics for tremolite cleavage fragments and fibers: U.S. Bureau of Mines Report of Investigations 8367, 18 p.	NA
Mineralogical	1980	Bates, R.L., and Jackson, J.A., eds., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.	**[cryst]** Said of a crystal that is needlelike in form. Cf: *fascicular; sagenitic.*

Table 1. Acicular

Community	Year	Source	Acicular
Mineralogical	1982	MacKenzie, W.S., Donaldson, C.H., and Guilford, C., 1982, Atlas of igneous rocks and their textures: New York, N.Y., Wiley, p. 20.	syn. Needle-like fibre, fibrous, hair-like
Mineralogical	1987	Dorling, M. and Zussman, J., 1987, Characteristics of asbestiform and non-asbestiform calcic amphiboles: Lithos, v. 20, p. 469-489.	needle-like
Mineralogical	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA
Mineralogical	1993	Klein, C. and Hurlbut, C.S., Jr. ,1993, Manual of mineralogy (after James D. Dana) (21st ed.): New York, N.Y., Wiley, 681 p.	Slender, needlelike crystals.
Mineralogical	1993	Veblen, D.R. and Wylie, A.G., 1993, Mineralogy of amphiboles and 1:1 layer silicates in Guthrie Jr., G.D. and Mossman, B.T., eds., Health effects of mineral dusts: Reviews in Mineralogy, v. 28, p. 61-137,	NA
Mineralogical	2001	Virta, R.L., 2001, Some facts about asbestos: U.S. Geological Survey Fact Sheet FS-012-01, 4 p.	As the length increases relative to the width, the crystals are called acicular.
Mineralogical	2002	http://webmineral.com/help/Fracture.html	NA
Mineralogical	2002	http://webmineral.com/help/Habits.html	Occurs as needle-like crystals.
Regulatory	1974	U.S. District Court, district of Minnesota, 5th Division. Supplemental Memorandum. No. 5-72, Civil 19, Appendix 5, May 11, 1974, p. 24	NA
Regulatory	1976	National Institute for Occupational Safety and Health, 1976, Revised recommended asbestos standard: DHEW (NIOSH) Publication No. 77-169, 96 p.	NA
Regulatory	1983	29 CFR 1910.1001	NA
Regulatory	1990	Ohio Administrative Code (OAC) 3745-20-01	NA

Table 1. Acicular

Community	Year	Source	Acicular
Regulatory	1992	Crane, D., 1992, Polarized light microscopy of asbestos: Occupational Safety and Health Administration Method # ID-191.	NA
Regulatory	1992	Occupational Safety and Health Administration, 1992, Preambles IV. Mineralogical Considerations, National Stone Association and American Mining Congress	NA
Regulatory	1993	Perkins, R.L. and Harvey, B.W., 1993, Method for the determination of asbestos in bulk building materials: U.S. Environmental Protection Agency EPA/600/R-93/116, Office of Research and Development, Washington, D.C.	NA
Regulatory	1993	Occupational Safety and Health Administration, 1993, Better protection against asbestos in the workplace: U.S. Department of Labor Fact Sheet No. OSHA 93-06. Available on the world wide web at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FACT_SHEETS&p_id=144	NA
Regulatory	1995	American Society for Testing and Materials, 1995, Standard test method for microvacuum sampling and indirect analysis of dust by transmission electron microscopy for asbestos structure number concentrations: West Conshohocken, Pa., ASTM 5755-95, 13 p.	NA
Regulatory	1995	International Organization for Standardization, 1995, ISO 10312 Ambient air-determination of asbestos fibres-direct-transfer transmission electron microscopy method (1st ed): Geneve, Switzerland, International Organization for Standardization, 51 p.	The shape of an extremely slender crystal with cross-sectional dimensions which are small relative to its length, i.e. needle-like.

Table 1. Acicular

Community	Year	Source	Acicular
Regulatory	1996	Colorado Air Quality Control Commission, 1996, Part B-emission standards for asbestos, *excerpted from* Regulation No. 8 "The control of hazardous air pollutants": Colorado Department of Public Health and Environment, 114 p.	NA
Regulatory	1997	Crane, D., 1997, Asbestos in air: Occupational Safety and Health Administration Method # ID-160.	NA
Regulatory	1997	NYCRR (New York Code of Rules & Regulations) Title 10 Section 73.1	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools (7-1-01 Edition)	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools Appendix A (7-1-01 Edition)	NA
Regulatory	2001	29 CFR 1910.1001	NA
Regulatory	2001	30 CFR 56.5001	NA
Regulatory	2001	17 CCR (California Code of Regulations) 93105	NA
Regulatory	2001	West Virginia Code 16-32-2	NA
Regulatory	2002	OAR (Oregon Administrative Rules) 340-248-0010	NA
Regulatory	2002	105 ILCS (Illinois Compiled Statutes Schools) 105/3	NA

Table 2. Asbestiform

Community	Year	Source	Asbestiform
Industrial	1975	Winson, R.W., 1975, Asbestos, *in*, Industrial minerals and rocks (nonmetallics other than fuels): New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 379-425.	NA
Industrial	1981	Steel, E. and Wylie, A., 1981, Mineralogical characteristics of asbestos *in* Riordon, P.H. ed, Geology of Asbestos Deposits, Society of Mining Engineers, p. 93-100.	The asbestiform habit is most commonly developed in certain amphiboles and chrysotile, but other minerals also may crystallize with this unusual habit. The habit may be characterized by (1) a fibril structure, single or twinned crystals of very small widths (generally less than 0.5 um), which have grown with a common fiber axis direction, but are disoriented in the other crystallographic directions; (2) anomalous optical properties, primarily parallel extinction; (3) unusual tensile strengths; (4) high aspect ratio; and (5) flexibility.
Industrial	1998	Virta, R.L., 2002, Asbestos: U.S. Geological Survey Open File-Report 02-149, 35 p.	NA
Interdisciplinary	1974	Thompson, C.S., 1974, Discussion of the mineralogy of industrial talcs: U.S. Bureau of Mines Information Circular 8639, p. 22-42.	NA
Interdisciplinary	1978	Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.	A special type of fibrous habit in which the fibers are separable, and are more flexible and possess higher tensile strength than crystals in other habits of the same mineral.
Interdisciplinary	1979	Chatfield, E.J., 1979, Measurement of asbestos fibres in the workplace and in the general environment *in* Ledoux, R.L., Mineralogical techniques of asbestos determination: Mineralogical Association of Canada Short Course, v. 4, p. 111-157.	NA
Interdisciplinary	1980	Dixon, W.C., 1980, Applications of optical microscopy in analysis of asbestos and quartz, *chap 2 of* Dollberg, D.D. and Werstuyft, A.W., eds., Analytical techniques in occupational health chemistry: Washington, D.C., American Chemical Society, p. 13-41.	NA

Table 2. Asbestiform

Community	Year	Source	Asbestiform
Interdisciplinary	1980	Clark, R.L., 1982, MSHA standard method for fiber identification by electron microscopy: National Bureau of Standards Special Publication 619, p. 207-210.	NA
Interdisciplinary	1980	Lee, R.J., Kelly, J.F., and Walker, J.S., 1982, Considerations in the analysis and definition of asbestos using electron microscopy: National Bureau of Standards Special Publication 619, p. 132-137.	NA
Interdisciplinary	1980	Chatfield, E.J. and Lewis, G.M., 1980, Development and application of an analytical technique for measurement of asbestos fibers in vermiculite: Scanning Electron Microscopy, p. 329-340.	NA
Interdisciplinary	1984	National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.	ASBESTIFORM HABIT refers to the unusual crystallization habit of a mineral when the crystals are thin, hairlike fibers. Historically, the definition of the asbestiform habit was based primarily on appearance, and the properties were only implied. At present, the definition of asbestiform habit is often augmented to include a statement on the properties of asbestiform fibers, i.e., shape; enhanced strength, flexibility, and durability; diameter-dependent strength; and unique surfaces. The fibers of asbestos are good examples of the asbestiform habit.
Interdisciplinary	1984	Cossette, M., 1984, Defining asbestos particulates for monitoring purposes in Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, p. 5-49.	...a mineral structured in the form of asbestos
Interdisciplinary	1984	Ross, M., Kuntze, R.A., and Clifton, R.A., 1984, A definition for asbestos in Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, pp.139-147.	NA

Table 2. Asbestiform

Community	Year	Source	Asbestiform
Interdisciplinary	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	An adjective used to describe inorganic materials that possess the form and appearance of asbestos (OED, WEB). Asbestine, asbestoid, and asbestos are obsolete synonyms. Asbestiform materials are a subset of fibrous materials. The term should be employed only when the material is one of the minerals mined as asbestos and possesses fibrosity typical of asbestos-that is, with relatively small fiber thickness, flexibility, separability, and general parallel arrangement of fibers en masse. The term asbestiform has also been used to imply that a sample or an individual fiber has morphological (gross external) characteristics similar to those of asbestos, but not necessarily the chemical or other physical properties of asbestos. In the 1700s asbestiform was used for the fibrous members of the amphibole group only. At that time virtually all asbestos in common use was amphibole-asbestos.
Interdisciplinary	1990	Mossman, B.T., Bignon, J., Corn, M., Seaton, A., and Gee, J.B.L., 1990, Asbestos-scientific developments and implications for public policy: Science, v. 247, p. 294-301.	NA
Interdisciplinary	2000	The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2000 by Houghton Mifflin Company.	NA
Interdisciplinary	2000	Wylie, A.G., 2000, The habit of asbestiform amphiboles: implications for the analysis of bulk samples in Beard, M.E. and Rooks, H.L, eds., Advances in environmental measurement methods for asbestos: ASTM Special Technical Publication 1342, p. 53-69.	NA

Table 2. Asbestiform

Community	Year	Source	Asbestiform
Interdisciplinary	2001	Beard, M.E., Crankshaw, O.S., Ennis, J.T., and Moore, C.E., 2001, Analysis of crayons for asbestos and other fibrous materials, and recommendations for improved analytical definitions: Research Triangle Park, North Carolina, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, Earth and Mineral Sciences Department, [informal report], 23 p., plus appendices A-H.	Asbestiform fibers are those having the crystal structure of the above minerals and having physical characteristics such as (1) mean aspect ratios (length to width) of 20:1 to 100:1 or greater for individual fibers; (2) very thin fibrils usually less than 0.5 um in width; (3) and parallel fibers in bundles with splayed ends, matted masses of fibers, and/or fibers showing curvature.
Interdisciplinary	2001	Nolan, R.P., Langer, A.M., Ross, M., Wicks, F.J., and Martin, R.F., eds., 2001, The health effects of chrysotile asbestos-contribution of science to risk-management decisions: The Canadian Mineralogist Special Publication 5, 304 p.	A term used to describe minerals that possess a habit and appearance similar to that displayed by asbestos.
Medical	1977	Zielhuis, R.L., 1977, Public health risks of exposure to asbestos: Elmsford, N.Y., Pergamon Press Inc., 143 p.	NA
Medical	1979	Langer, A.M., Rohl, A.N., Wolff, M., and Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments-Nomenclature and biological properties, in Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.	...denotes an asbestos variety of silicate fiber; it may be used as a synonym for asbestos (Campbell et al., 1979; Zoltai, 1978). Although recommended, a current dictionary of geological terms suggests that asbestiform may be used to describe fibers which merely resemble asbestos (Thrush, 1978)
Medical	1998	Blake, T., Castranova, V., Schwegler-Berry, D., Baron, P., Deye, G.J., Li, C., and Jones, W., 1998, Effect of fiber length on glass microfiber cytotoxicity: Journal of Toxicology and Environmental Health, v. 54, p. 243-259.	NA
Medical	2001	Ninth Report on Carcinogens, January 2001 http://ehp.niehs.nih.gov/roc/ninth/known/asbestos.pdf	NA

Table 2. Asbestiform

Community	Year	Source	Asbestiform
Mineralogical	1914	Dana, E.S., 1914, The system of mineralogy of James Dwight Dana, descriptive mineralogy (6th ed): New York, N.Y., Wiley, p.	NA
Mineralogical	1977	Campbell, W.J., Blake, R.L, Brown, L.L., Cather, E.E., and Sjober, J.J., 1977, Selected silicate minerals and their asbestiform varieties: U.S. Bureau of Mines Information Circular 8751, 56 p.	A specific type of mineral fibrosity in which the fibers and fibrils posses high tensile strength and flexibility.
Mineralogical	1979	Campbell, W.J., Steel, E.B., Virta, R.L., and Eisner, M.H., 1979, Relationship of mineral habit to size characteristics for tremolite cleavage fragments and fibers: U.S. Bureau of Mines Report of Investigations 8367, 18 p.	NA
Mineralogical	1980	Bates, R.L., and Jackson, J.A., eds., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.	Said of a mineral that is fibrous, i.e. that is like asbestos.
Mineralogical	1982	MacKenzie, W.S., Donaldson, C.H., and Guilford, C., 1982, Atlas of igneous rocks and their textures: New York, N.Y., Wiley, p. 20.	NA
Mineralogical	1987	Dorling, M. and Zussman, J., 1987, Characteristics of asbestiform and non-asbestiform calcic amphiboles: Lithos, v. 20, p. 469-489.	NA
Mineralogical	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA
Mineralogical	1993	Klein, C. and Hurlbut, C.S., Jr. ,1993, Manual of mineralogy (after James D. Dana) (21st ed.): New York, N.Y., Wiley, 681 p.	The term asbestiform refers to minerals that are mined as asbestos and possess fibrosity typical of asbestos-that is, with small fiber thickness, flexibility, and separability.

Table 2. Asbestiform

Community	Year	Source	Asbestiform
Mineralogical	1993	Veblen, D.R. and Wylie, A.G., 1993, Mineralogy of amphiboles and 1:1 layer silicates in Guthrie Jr., G.D. and Mossman, B.T., eds., Health effects of mineral dusts: Reviews in Mineralogy, v. 28, p. 61-137,	...any mineral resembling asbestos is asbestiform
Mineralogical	2001	Virta, R.L., 2001, Some facts about asbestos: U.S. Geological Survey Fact Sheet FS-012-01, 4 p.	When the length is extremely long compared with the width, the crystals are called asbestiform or fibrous.
Mineralogical	2002	http://webmineral.com/help/Fracture.html	NA
Mineralogical	2002	http://webmineral.com/help/Habits.html	NA
Regulatory	1974	U.S. District Court, district of Minnesota, 5th Division. Supplemental Memorandum. No. 5-72, Civil 19, Appendix 5, May 11, 1974, p. 24	NA
Regulatory	1976	National Institute for Occupational Safety and Health, 1976, Revised recommended asbestos standard: DHEW (NIOSH) Publication No. 77-169, 96 p.	NA
Regulatory	1983	29 CFR 1910.1001	NA
Regulatory	1990	Ohio Administrative Code (OAC) 3745-20-01	NA
Regulatory	1992	Crane, D., 1992, Polarized light microscopy of asbestos: Occupational Safety and Health Administration Method # ID-191.	NA
Regulatory	1992	Occupational Safety and Health Administration, 1992, Preambles IV. Mineralogical Considerations, National Stone Association and American Mining Congress	The asbestiform habit can be defined as a habit where mineral crystals grow in a single dimension, in a straight line until they form long, thread-like fibers with aspect ratios of 20:1 to 100:1 and higher.

Table 2. Asbestiform

Community	Year	Source	Asbestiform
Regulatory	1993	Perkins, R.L. and Harvey, B.W., 1993, Method for the determination of asbestos in bulk building materials: U.S. Environmental Protection Agency EPA/600/R-93/116, Office of Research and Development, Washington, D.C.	(morphology) Said of a mineral that is like asbestos, i.e., crystallized with the habit of asbestos. Some asbestiform minerals may lack the properties which make asbestos commercially valuable, such as long fiber length and high tensile strength. With the light microscope, the asbestiform habit is generally recognized by the following characteristics: 1) Mean aspect ratios ranging from 20:1 to 100:1 or higher for fibers longer than 5 um. Aspect ratios should be determined for fibers, not bundles. 2) Very thin fibrils, usually less than 0.5 micrometers in width, and 3) Two or more of the following: a) Parallel fibers occurring in bundles, b) Fiber bundles displaying splayed ends, c) matted masses of individual fibers, and/or d) Fibers showing curvature. These characteristics refer to the population of fibers as observed in a bulk sample. It is not unusual to observe occasional particles having aspect ratios of 10:1 or less, but it is unlikely that the asbestos component(s) would be dominated by particles (individual fibers) having aspect ratios of <20:1 for fibers longer than 5um. If a sample contains a fibrous component of which most of the fibers have aspect ratios of <20:1 and that do not display the additional asbestiform characteristics, by definition the component should not be considered asbestos.
Regulatory	1993	Occupational Safety and Health Administration, 1993, Better protection against asbestos in the workplace: U.S. Department of Labor Fact Sheet No. OSHA 93-06. Available on the world wide web at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FACT_SHEETS&p_id=144	NA
Regulatory	1995	American Society for Testing and Materials, 1995, Standard test method for microvacuum sampling and indirect analysis of dust by transmission electron microscopy for asbestos structure number concentrations: West Conshohocken, Pa., ASTM 5755-95, 13 p.	a special type of fibrous habit in which the fibers are separable into thinner fibers and ultimately into fibrils. This habit accounts for greater flexibility and higher tensile strength than other habits of the same mineral.

Table 2. Asbestiform

Community	Year	Source	Asbestiform
Regulatory	1995	International Organization for Standardization, 1995, ISO 10312 Ambient air-determination of asbestos fibres-direct-transfer transmission electron microscopy method (1st ed): Geneve, Switzerland, International Organization for Standardization, 51 p.	A specific type of mineral fibrosity in which the fibres and fibrils posses high tensile strength and flexibility.
Regulatory	1996	Colorado Air Quality Control Commission, 1996, Part B-emission standards for asbestos, *excerpted from* Regulation No. 8 "The control of hazardous air pollutants": Colorado Department of Public Health and Environment, 114 p.	NA
Regulatory	1997	Crane, D., 1997, Asbestos in air: Occupational Safety and Health Administration Method # ID-160.	NA
Regulatory	1997	NYCRR (New York Code of Rules & Regulations) Title 10 Section 73.1	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools (7-1-01 Edition)	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools Appendix A (7-1-01 Edition)	A specific type of mineral fibrosity in which the fibers and fibrils possess high tensile strength and flexibility
Regulatory	2001	29 CFR 1910.1001	NA
Regulatory	2001	30 CFR 56.5001	NA
Regulatory	2001	17 CCR (California Code of Regulations) 93105	NA
Regulatory	2001	West Virginia Code 16-32-2	NA
Regulatory	2002	OAR (Oregon Administrative Rules) 340-248-0010	NA
Regulatory	2002	105 ILCS (Illinois Compiled Statutes Schools) 105/3	NA

Table 3. Asbestos

Community	Year	Source	Asbestos
Industrial	1975	Winson, R.W., 1975, Asbestos, *in*, Industrial minerals and rocks (nonmetallics other than fuels): New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 379-425.	...is a generic name given to a group of fibrous mineral silicates found in nature. They are all incombustible and can be separated by mechanical means into fibers of various lengths and cross sections, but each differs in chemical composition from the other.
Industrial	1981	Steel, E. and Wylie, A., 1981, Mineralogical characteristics of asbestos *in* Riordon, P.H. ed, Geology of Asbestos Deposits, Society of Mining Engineers, p. 93-100.	NA
Industrial	1998	Virta, R.L., 2002, Asbestos: U.S. Geological Survey Open File-Report 02-149, 35 p.	...is a generic name given to six fibrous minerals that have been used in commercial products. The six types of asbestos are chrysotile, the most widely used; crocidolite; amosite; anthophyllite asbestos; tremolite asbestos; and actinolite asbestos. The properties that make asbestos so versatile and cost effective are high tensile strength, chemical and thermal stability, high flexibility, low electrical conductivity, and larger surface area.
Interdisciplinary	1974	Thompson, C.S., 1974, Discussion of the mineralogy of industrial talcs: U.S. Bureau of Mines Information Circular 8639, p. 22-42.	The term "asbestos" is a nonscientific commercial term normally restricted in use to the long, threadlike fibrous varieties of several hydrated silicate minerals, whose fibers can be separated mechanically and pressed, spun, or woven into articles of all types that are resistant to heat and chemical alteration. Although present usage is generally limited to the commercially available silicate minerals, chrysotile, crocidolite, amosite, anthophyllite asbestos, tremolite asbestos, and actinolite asbestos, other minerals regardless of chemical composition, which posses similar qualities of great elongation, flexibility, high-tensile strength, heat and chemical resistance, spinability, etc., could properly be classified as asbestos.
Interdisciplinary	1978	Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.	A collective mineralogical term which includes the asbestiform varieties of various (silicate) minerals.

Table 3. Asbestos

Community	Year	Source	Asbestos
Interdisciplinary	1979	Chatfield, E.J., 1979, Measurement of asbestos fibres in the workplace and in the general environment *in* Ledoux, R.L., Mineralogical techniques of asbestos determination: Mineralogical Association of Canada Short Course, v. 4, p. 111-157.	Asbestos is a term used to describe a number of minerals which have the property that they can be separated into long silky fibres.
Interdisciplinary	1980	Dixon, W.C., 1980, Applications of optical microscopy in analysis of asbestos and quartz, *chap 2 of* Dollberg, D.D. and Werstuyft, A.W., eds., Analytical techniques in occupational health chemistry: Washington, D.C., American Chemical Society, p. 13-41.	[*Author quotes the federal register*] 1. Asbestos includes chrysotile, amosite, crocidolite, tremolite, anthophyllite and actinolite. 2. "Asbestos fibers" means asbestos fibers longer than 5 micrometers.
Interdisciplinary	1980	Clark, R.L., 1982, MSHA standard method for fiber identification by electron microscopy: National Bureau of Standards Special Publication 619, p. 207-210.	[*uses Code of Federal Regulations*] "asbestos" is recognized as generic, applicable to a number of hydrated silicates, but its use is specifically limited to describe the minerals chrysotile, amosite, crocidolite, anthophyllite asbestos, tremolite asbestos, and actinolite asbestos.
Interdisciplinary	1980	Lee, R.J., Kelly, J.F., and Walker, J.S., 1982, Considerations in the analysis and definition of asbestos using electron microscopy: National Bureau of Standards Special Publication 619, p. 132-137.	...meaningful working definition of asbestos, we propose the following: 1. For routine method, a minimum aspect ratio of 10:1 should be used in a screening analysis or survey. Existing data indicate that this would not affect the chrysotile analysis at all and amphibole analysis only when the sample contains a significant percentage of acicular nonasbestos particles [11-16]. While this would undoubtedly result in missing 5 to 20 percent of the short asbestos particles, it would eliminate 70 to 80 percent of the nonasbestos particles from consideration. 2. A lower length limit for routine electron microscope analysis should be adopted. On the basis of available information, a reasonable limit would be somewhere between 0.75 and 2.0 microns [3]. 3. Asbestos analyses should be grouped into at least three size fractions and acceptable uncertainty levels defined for each range. For example, the length categories less than 2, 2 to 5, and greater than 5 um might be chosen, and a 50 percent relative error defined as the minimum level of acceptance for each size range.

Table 3. Asbestos

Community	Year	Source	Asbestos
Interdisciplinary	1980	Chatfield, E.J. and Lewis, G.M., 1980, Development and application of an analytical technique for measurement of asbestos fibers in vermiculite: Scanning Electron Microscopy, p. 329-340.	NA
Interdisciplinary	1984	National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.	The term ASBESTOS is a commercial-industrial term rather than a mineralogical term. It refers to well-developed and hairlike long-fibered varieties of certain minerals that satisfy particular industrial needs. Table 2-1 lists the names of chemical formulas of the minerals included in the term asbestos. Other minerals used in industry, such as palygorskite, may also crystallize as well-developed, thin hairlike fibers (i.e., in the asbestiform habit), but they are not called asbestos. [*Minerals listed in Table 2-1: chrysotile, riebeckite, anthophyllite, cummingtonite-grunerite, actinolite-tremolite*]
Interdisciplinary	1984	Cossette, M., 1984, Defining asbestos particulates for monitoring purposes *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, p. 5-49.	...a generic term for naturally occurring inorganic hydrated silicates, occurring in layered structures composed of chains of silicon/oxygen tetrahedra, which can subdivide into flexible fibers
Interdisciplinary	1984	Ross, M., Kuntze, R.A., and Clifton, R.A., 1984, A definition for asbestos *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, pp.139-147.	...a term applied to six naturally occurring minerals exploited commercially for their desirable physical properties, which are in part derived from their asbestiform habit. The six minerals are the serpentine mineral chrysotile and the amphibole minerals grunerite asbestos (also referred to as amosite), riebeckite asbestos (also referred to as crocidolite), anthophyllite asbestos, tremolite asbestos, and actinolite asbestos... Individual mineral particles, however processed and regardless of their mineral name, are not demonstrated to be asbestos if the length-to-width ratio is less than 20:1.

Table 3. Asbestos

Community	Year	Source	Asbestos
Interdisciplinary	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	A commercial and generally used name for fibrous varieties of naturally occurring silicate minerals of the amphibole or serpentine group (see chapter 2). Over the millennia many fibrous minerals have been called asbestos, including the six minerals presently accepted (see in the following), as well as other silicates such as palygorskite and nonsilicates such as brucite. The characteristics of mineral materials that have invoked the use of the term asbestos are: slender fibers that are easily separable and flexible, and fine fibers that have high tensile strength, chemical stability, and are incombustible. Natural unprocessed asbestos fibers have large aspect ratios and may have lengths of microscopic dimensions up to, in rare instances, a meter or so. Chrysotile-asbestos fibers are commonly 10 centimeters in length...Asbestos is used as an adjective in combination with numerous other words and phases, such as asbestos cement.
Interdisciplinary	1990	Mossman, B.T., Bignon, J., Corn, M., Seaton, A., and Gee, J.B.L., 1990, Asbestos-scientific developments and implications for public policy: Science, v. 247, p. 294-301.	"Asbestos" is a broad commercial term for a group of naturally occurring hydrated silicates that crystallize in a fibrous habit.
Interdisciplinary	2000	The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2000 by Houghton Mifflin Company.	n. Either of two incombustible, chemical-resistant, fibrous mineral forms of impure magnesium silicate, used for fireproofing, electrical insulation, building materials, brake linings, and chemical filters.
Interdisciplinary	2000	Wylie, A.G., 2000, The habit of asbestiform amphiboles: implications for the analysis of bulk samples *in* Beard, M.E. and Rooks, H.L, eds., Advances in environmental measurement methods for asbestos: ASTM Special Technical Publication 1342, p. 53-69.	NA

Table 3. Asbestos

Community	Year	Source	Asbestos
Interdisciplinary	2001	Beard, M.E., Crankshaw, O.S., Ennis, J.T., and Moore, C.E., 2001, Analysis of crayons for asbestos and other fibrous materials, and recommendations for improved analytical definitions: Research Triangle Park, North Carolina, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, Earth and Mineral Sciences Department, [informal report], 23 p., plus appendices A-H.	Asbestos is a commercial term for long, thin mineral fibers of chrysotile, amosite, crocidolite, anthophyllite, tremolite, and actinolite.
Interdisciplinary	2001	Nolan, R.P., Langer, A.M., Ross, M., Wicks, F.J., and Martin, R.F., eds., 2001, The health effects of chrysotile asbestos-contribution of science to risk-management decisions: The Canadian Mineralogist Special Publication 5, 304 p.	A commercial term that describes a group of extremely thin and flexible minerals that have a unique combination of physical and chemical properties. The long asbestos fibers can be spun in yarn and then made into woven fabric. Asbestos is derived from a Greek word meaning inextinguishable in the sense of indestructible, because asbestos cannot be destroyed by fire. Modern usage in mineralogy occurred when the term was applied to a fibrous amphibole mineral discovered in the Alps.
Medical	1977	Zielhuis, R.L., 1977, Public health risks of exposure to asbestos: Elmsford, N.Y., Pergamon Press Inc., 143 p.	Asbestos refers to a group of inorganic silicates which occur naturally and have a distinct fibrous crystalline structure, which is largely responsible for its unique properties: tensile strength, stiffness, heat resistance, and ability to split into finer fibres.
Medical	1979	Langer, A.M., Rohl, A.N., Wolff, M., and Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments-Nomenclature and biological properties, in Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.	The term "asbestos" may be used to describe a mineral species only when its physical characteristics, on the megascopic level, are known: the mineral fiber possesses tensile strength, flexibility, and those other characteristics which distinguishes asbestiform minerals from their rock-forming analogues. Asbestos may also be applied to submicroscopic fibers if the source materials are known; for example, in an asbestos textile factory where chrysotile fiber is used.
Medical	1998	Blake, T., Castranova, V., Schwegler-Berry, D., Baron, P., Deye, G.J., Li, C., and Jones, W., 1998, Effect of fiber length on glass microfiber cytotoxicity: Journal of Toxicology and Environmental Health, v. 54, p. 243-259.	...refers to a group of naturally occurring fibrous metallic silicates that have been used widely in construction and industry.

Table 3. Asbestos

Community	Year	Source	Asbestos
Medical	2001	Ninth Report on Carcinogens, January 2001 http://ehp.niehs.nih.gov/roc/ninth/known/asbestos.pdf	...is a generic name given to a class of natural fibrous silicates that vary considerably in their physical and chemical properties.
Mineralogical	1914	Dana, E.S., 1914, The system of mineralogy of James Dwight Dana, descriptive mineralogy (6th ed): New York, N.Y., Wiley, p.	Asbestus. Asbestos. Tremolite, actinolite, and other varieties of amphibole, excepting those containing much alumina, pass into fibrous varieties, the fibers of which are sometimes very long, fine, flexible, and easily separable by the fingers and look like flax. These kinds are called asbestus.
Mineralogical	1977	Campbell, W.J., Blake, R.L, Brown, L.L., Cather, E.E., and Sjober, J.J., 1977, Selected silicate minerals and their asbestiform varieties: U.S. Bureau of Mines Information Circular 8751, 56 p.	(1) A collective mineralogical term encompassing the asbestiform varieties of various minerals; (2) an industrial product obtained by mining and processing primarily asbestiform minerals.
Mineralogical	1979	Campbell, W.J., Steel, E.B., Virta, R.L., and Eisner, M.H., 1979, Relationship of mineral habit to size characteristics for tremolite cleavage fragments and fibers: U.S. Bureau of Mines Report of Investigations 8367, 18 p.	NA
Mineralogical	1980	Bates, R.L., and Jackson, J.A., eds., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.	(a) A commercial term applied to a group of highly fibrous silicate minerals that readily separate into long, thin, strong fibers of sufficient flexibility to be woven, are heat resistant and chemically inert, and possess a high electric insulation, and therefore are suitable for uses (as in yarn, cloth, paper, paint, brake linings, tiles, insulation, cement, fillers, and filters) where incombustible, nonconducting, or chemically resistant material is required. (b) A mineral of the asbestos group, principally chrysotile (best adapted for spinning) and certain fibrous varieties of amphibole (esp. tremolite, actinolite, and crocidolite). (c) A term strictly applied to the fibrous variety of actinolite.—Syn: *asbestus; amianthus; earth flax; mountain flax.*
Mineralogical	1982	MacKenzie, W.S., Donaldson, C.H., and Guilford, C., 1982, Atlas of igneous rocks and their textures: New York, N.Y., Wiley, p. 20.	NA
Mineralogical	1987	Dorling, M. and Zussman, J., 1987, Characteristics of asbestiform and non-asbestiform calcic amphiboles: Lithos, v. 20, p. 469-489.	In this study, only specimens [*in reference to calcic amphiboles*] which occur as bundles of fibres (commonly having splayed ends), which readily split into still finer sub-microscopic units (fibrils), are referred to and are classed as asbestos.

Table 3. Asbestos

Community	Year	Source	Asbestos
Mineralogical	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA
Mineralogical	1993	Klein, C. and Hurlbut, C.S., Jr. ,1993, Manual of mineralogy (after James D. Dana) (21st ed.): New York, N.Y., Wiley, 681 p.	The characteristic morphology of all asbestos minerals, in their natural form, is a parallel-sided fiber with a length to width ratio (referred to as an aspect ratio) in excess of 100:1 (Champness, P.E., Cliff, G. and Lorimer, G.W., 1976, The identification of asbestos, *Journal of Microscopy*, v. 108, pp. 231-249).
Mineralogical	1993	Veblen, D.R. and Wylie, A.G., 1993, Mineralogy of amphiboles and 1:1 layer silicates in Guthrie Jr., G.D. and Mossman, B.T., eds., Health effects of mineral dusts: Reviews in Mineralogy, v. 28, p. 61-137,	Asbestos is defined as a group of highly fibrous silicate minerals that readily separate into long, thin, strong fibers that have sufficient flexibility to be woven, are heat resistant and chemically inert, are electrical insulators, and therefore are suitable for uses where incombustible, nonconducting, or chemically resistant material is required.
Mineralogical	2001	Virta, R.L., 2001, Some facts about asbestos: U.S. Geological Survey Fact Sheet FS-012-01, 4 p.	...is a generic name given to the fibrous variety of six naturally occurring minerals that have been used in commercial products. Asbestos is made up of fiber bundles. These bundles, in turn, are composed of extremely long and thin fibers that can be easily separated from one another. The bundles have splaying ends and are extremely flexible. The term "asbestos" is not a mineralogical definition. It is a commercial designation for mineral products that possess high tensile strength, flexibility, resistance to chemical and thermal degradation, and high electrical resistance and that can be woven.
Mineralogical	2002	http://webmineral.com/help/Fracture.html	NA
Mineralogical	2002	http://webmineral.com/help/Habits.html	NA
Regulatory	1974	U.S. District Court, district of Minnesota, 5th Division. Supplemental Memorandum. No. 5-72, Civil 19, Appendix 5, May 11, 1974, p. 24	...is a generic term for a number of hydrated silicates that, when crushed or processed, separate into flexible fibers made up of fibrils.
Regulatory	1976	National Institute for Occupational Safety and Health, 1976, Revised recommended asbestos standard: DHEW (NIOSH) Publication No. 77-169, 96 p.	Asbestos fibers are defined as those particles with a length greater than 5 um and a length-to-diameter ratio of 3:1, or greater.
Regulatory	1983	29 CFR 1910.1001	For the purpose of this section, (1) "Asbestos" includes chrysotile, amosite, crocidolite, tremolite, anthophyllite, and actinolite.

Table 3. Asbestos

Community	Year	Source	Asbestos
Regulatory	1990	Ohio Administrative Code (OAC) 3745-20-01	"Asbestos" means the asbestiform varieties of serpentinite (chrysotile), riebeckite (crocidolite), cummingtonite-grunerite, anthophyllite, and actinolite tremolite.
Regulatory	1992	Crane, D., 1992, Polarized light microscopy of asbestos: Occupational Safety and Health Administration Method # ID-191.	A term for naturally occurring fibrous minerals. Asbestos includes chrysotile, cummingtonite-grunerite asbestos (amosite), anthophyllite asbestos, tremolite asbestos, crocidolite, actinolite asbestos and any of these minerals which have been chemically treated or altered. The precise chemical formulation of each species varies with the location from which it was mined.
Regulatory	1992	Occupational Safety and Health Administration, 1992, Preambles IV. Mineralogical Considerations, National Stone Association and American Mining Congress	NA
Regulatory	1993	Perkins, R.L. and Harvey, B.W., 1993, Method for the determination of asbestos in bulk building materials: U.S. Environmental Protection Agency EPA/600/R-93/116, Office of Research and Development, Washington, D.C.	A commercial term applied to the asbestiform varieties of six different minerals. The asbestos types are chrysotile (asbestiform serpentine), amosite (asbestiform grunerite), crocidolite (asbestiform riebeckite), and asbestiform anthophyllite, asbestiform tremolite, and asbestiform actinolite. The properties of asbestos that caused it to be widely used commercially are: 1) its ability to be separated into long, thin flexible fibers; 2) high tensile strength; 3) low thermal and electrical conductivity; 4) high mechanical and chemical durability, and 5) high heat resistance.
Regulatory	1993	Occupational Safety and Health Administration, 1993, Better protection against asbestos in the workplace: U.S. Department of Labor Fact Sheet No. OSHA 93-06. Available on the world wide web at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FACT_SHEETS&p_id=144	...is a widely used, mineral-based material that is resistant to heat and corrosive chemicals. Typically, asbestos appears as a whitish, fibrous material which may release fibers that range in texture from coarse to silky; however, airborne fibers that can cause health damage may be too small to see with the naked eye.
Regulatory	1995	American Society for Testing and Materials, 1995, Standard test method for microvacuum sampling and indirect analysis of dust by transmission electron microscopy for asbestos structure number concentrations: West Conshohocken, Pa., ASTM 5755-95, 13 p.	...a collective term that describes a group of naturally occurring, inorganic, highly fibrous, silicate dominated minerals, which are easily separated into long, thin, flexible fibers when crushed or processed.

Table 3. Asbestos

Community	Year	Source	Asbestos
Regulatory	1995	International Organization for Standardization, 1995, ISO 10312 Ambient air-determination of asbestos fibres-direct-transfer transmission electron microscopy method (1st ed): Geneve, Switzerland, International Organization for Standardization, 51 p.	A term applied to a group of silicate minerals belonging to the serpentine and amphibole groups which have crystallized in the asbestiform habit, causing them to be easily separated into long, thin, strong fibres when crushed or processed. The Chemical Abstracts Service Registry Numbers of the common asbestos varieties are: chrysotile (12001-29-5), crocidolite (12001-28-4), grunerite asbestos (amosite) (12172-73-5), anthophyllite asbestos (77536-67-5), tremolite asbestos (77536-68-6) and actinolite asbestos (77536-66-4).
Regulatory	1996	Colorado Air Quality Control Commission, 1996, Part B-emission standards for asbestos, *excerpted from* Regulation No. 8 "The control of hazardous air pollutants": Colorado Department of Public Health and Environment, 114 p.	means asbestiform varieties of chrysotile, amosite (cummingtonite-grunerite), crocidolite, anthophyllite, tremolite, and actinolite.
Regulatory	1997	Crane, D., 1997, Asbestos in air: Occupational Safety and Health Administration Method # ID-160.	A term for naturally occurring fibrous minerals. Asbestos includes chrysotile, cummingtonite-grunerite asbestos (amosite), anthophyllite asbestos, tremolite asbestos, crocidolite, actinolite asbestos and any of these minerals which have been chemically treated or altered. The precise chemical formulation of each species varies with the location from which it was mined...
Regulatory	1997	NYCRR (New York Code of Rules & Regulations) Title 10 Section 73.1	Asbestos. Any naturally occurring hydrated mineral silicate separable into commercially usable fibers, including chrysotile (serpentine), amosite (cummingtonite-grunerite), crocidolite (riebeckite), tremolite, anthophyllite and actinolite.
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E—Asbestos-Containing Materials in Schools (7-1-01 Edition)	...means the asbestiform varieties of: Chrysotile (serpentine); crocidolite (riebeckite); amosite (cummingtonite-grunerite); anthophyllite; tremolite; and actinolite.
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E—Asbestos-Containing Materials in Schools Appendix A (7-1-01 Edition)	NA
Regulatory	2001	29 CFR 1910.1001	Asbestos includes chrysotile, amosite, crocidolite, tremolite asbestos, anthophyllite asbestos, actinolite asbestos, and any of these minerals that have been chemically treated and/or altered.

Table 3. Asbestos

Community	Year	Source	Asbestos
Regulatory	2001	30 CFR 56.5001	..."Asbestos" is a generic term for a number of hydrated silicates that, when crushed or processed, separate into flexible fibers made up of fibrils. Although there are many asbestos minerals, the term "asbestos" as used herein is limited to the following minerals: chrysotile, amosite, crocidolite, anthophyllite asbestos, tremolite asbestos, and actinolite asbestos.
Regulatory	2001	17 CCR (California Code of Regulations) 93105	"Asbestos" means asbestiforms* of the following minerals: chrysotile (fibrous serpentine), crocidolite (fibrous riebeckite), amosite (fibrous cummingtonite--grunerite), fibrous tremolite, fibrous actinolite, and fibrous anthophyllite. *[It is assumed that the authors of the above entry intended for the word "asbestiforms" to be interpreted as asbestiform varieties of these minerals. This unusual application of the term would probably not be considered appropriate by most workers in the mineralogical community.]
Regulatory	2001	West Virginia Code 16-32-2	Asbestos means the asbestiform varieties of chrysotile (serpentine), crocidolite (riebeckite), amosite (cummingtonite-grunerite), anthophyllite, tremolite and actinolite.
Regulatory	2002	OAR (Oregon Administrative Rules) 340-248-0010	"Asbestos" means the asbestiform varieties of serpentine (chrysotile), riebeckite (crocidolite), cummingtonite-grunerite (amosite), anthophyllite, actinolite and tremolite.
Regulatory	2002	105 ILCS (Illinois Compiled Statutes Schools) 105/3	"Asbestos" means the asbestiform varieties of chrysotile, amosite, crocidolite, tremolite, anthophyllite, and actinolite.

Table 4. Cleavage

Community	Year	Source	Cleavage
Industrial	1975	Winson, R.W., 1975, Asbestos, *in*, Industrial minerals and rocks (nonmetallics other than fuels): New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 379-425.	NA
Industrial	1981	Steel, E. and Wylie, A., 1981, Mineralogical characteristics of asbestos *in* Riordon, P.H. ed, Geology of Asbestos Deposits, Society of Mining Engineers, p. 93-100.	NA
Industrial	1998	Virta, R.L., 2002, Asbestos: U.S. Geological Survey Open File-Report 02-149, 35 p.	NA
Interdisciplinary	1974	Thompson, C.S., 1974, Discussion of the mineralogy of industrial talcs: U.S. Bureau of Mines Information Circular 8639, p. 22-42.	NA
Interdisciplinary	1978	Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.	NA
Interdisciplinary	1979	Chatfield, E.J., 1979, Measurement of asbestos fibres in the workplace and in the general environment *in* Ledoux, R.L., Mineralogical techniques of asbestos determination: Mineralogical Association of Canada Short Course, v. 4, p. 111-157.	NA
Interdisciplinary	1980	Dixon, W.C., 1980, Applications of optical microscopy in analysis of asbestos and quartz, *chap 2 of* Dollberg, D.D. and Werstuyft, A.W., eds., Analytical techniques in occupational health chemistry: Washington, D.C., American Chemical Society, p. 13-41.	A mineral has cleavage if it breaks along definite plane surfaces.
Interdisciplinary	1980	Clark, R.L., 1982, MSHA standard method for fiber identification by electron microscopy: National Bureau of Standards Special Publication 619, p. 207-210.	NA

Table 4. Cleavage

Community	Year	Source	Cleavage
Interdisciplinary	1980	Lee, R.J., Kelly, J.F., and Walker, J.S., 1982, Considerations in the analysis and definition of asbestos using electron microscopy: National Bureau of Standards Special Publication 619, p. 132-137.	NA
Interdisciplinary	1980	Chatfield, E.J. and Lewis, G.M., 1980, Development and application of an analytical technique for measurement of asbestos fibers in vermiculite: Scanning Electron Microscopy, p. 329-340.	NA
Interdisciplinary	1984	National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.	CLEAVAGE refers to the preferential breakage of crystals along certain planes of structural weakness. Such planes of weakness are called cleavage planes. A mineral with two distinct cleavage planes will preferentially fracture along these planes and will produce ACICULAR fragments...The strength and flexibility of cleavage fragments are approximately the same as those of single crystals. Cleavage cannot produce the high strength and flexibility of asbestiform fibers.
Interdisciplinary	1984	Cossette, M., 1984, Defining asbestos particulates for monitoring purposes *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, p. 5-49.	NA
Interdisciplinary	1984	Ross, M., Kuntze, R.A., and Clifton, R.A., 1984, A definition for asbestos *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, pp.139-147.	NA
Interdisciplinary	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	The property of an individual crystal to fracture or break, producing planar surfaces along specific crystallographic directions dictated by the structure of the material. Some crystals lack cleavage; others possess one or more crystallographically distinct cleavage directions (see chapter 1).
Interdisciplinary	1990	Mossman, B.T., Bignon, J., Corn, M., Seaton, A., and Gee, J.B.L., 1990, Asbestos-scientific developments and implications for public policy: Science, v. 247, p. 294-301.	NA

Table 4. Cleavage

Community	Year	Source	Cleavage
Interdisciplinary	2000	The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2000 by Houghton Mifflin Company.	1. Mineralogy. The splitting or tendency to split of a crystallized substance along definite crystalline planes, yielding smooth surfaces.
Interdisciplinary	2000	Wylie, A.G., 2000, The habit of asbestiform amphiboles: implications for the analysis of bulk samples *in* Beard, M.E. and Rooks, H.L, eds., Advances in environmental measurement methods for asbestos: ASTM Special Technical Publication 1342, p. 53-69.	weakness inherent in a "perfect" structure
Interdisciplinary	2001	Beard, M.E., Crankshaw, O.S., Ennis, J.T., and Moore, C.E., 2001, Analysis of crayons for asbestos and other fibrous materials, and recommendations for improved analytical definitions: Research Triangle Park, North Carolina, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, Earth and Mineral Sciences Department, [informal report], 23 p., plus appendices A-H.	NA
Interdisciplinary	2001	Nolan, R.P., Langer, A.M., Ross, M., Wicks, F.J., and Martin, R.F., eds., 2001, The health effects of chrysotile asbestos-contribution of science to risk-management decisions: The Canadian Mineralogist Special Publication 5, 304 p.	NA
Medical	1977	Zielhuis, R.L., 1977, Public health risks of exposure to asbestos: Elmsford, N.Y., Pergamon Press Inc., 143 p.	NA
Medical	1979	Langer, A.M., Rohl, A.N., Wolff, M., and Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments- Nomenclature and biological properties, *in* Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.	...in minerals is normally defined as planar separation occurring along crystallographic planes with the lowest surface energies.

Table 4. Cleavage

Community	Year	Source	Cleavage
Medical	1998	Blake, T., Castranova, V., Schwegler-Berry, D., Baron, P., Deye, G.J., Li, C., and Jones, W., 1998, Effect of fiber length on glass microfiber cytotoxicity: Journal of Toxicology and Environmental Health, v. 54, p. 243-259.	NA
Medical	2001	Ninth Report on Carcinogens, January 2001 http://ehp.niehs.nih.gov/roc/ninth/known/asbestos.pdf	NA
Mineralogical	1914	Dana, E.S., 1914, The system of mineralogy of James Dwight Dana, descriptive mineralogy (6th ed): New York, N.Y., Wiley, p.	...is a fracture yielding a more or less smooth surface in the crystal, usually along one of the principal planes of the lattice. The cleavage is characterized by the plane, the ease of production and the character of the surface
Mineralogical	1977	Campbell, W.J., Blake, R.L, Brown, L.L., Cather, E.E., and Sjober, J.J., 1977, Selected silicate minerals and their asbestiform varieties: U.S. Bureau of Mines Information Circular 8751, 56 p.	The tendency of a crystal to break in definite directions that are related to the crystal structure and are always parallel to possible crystal faces.
Mineralogical	1979	Campbell, W.J., Steel, E.B., Virta, R.L., and Eisner, M.H., 1979, Relationship of mineral habit to size characteristics for tremolite cleavage fragments and fibers: U.S. Bureau of Mines Report of Investigations 8367, 18 p.	NA
Mineralogical	1980	Bates, R.L., and Jackson, J.A., eds., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.	[mineral] The breaking of a mineral along its crystallographic planes, thus reflecting crystal structure. The types of cleavage are named according to the structure, e.g. prismatic cleavage. Cf: fracture [mineral]; parting [cryst].
Mineralogical	1982	MacKenzie, W.S., Donaldson, C.H., and Guilford, C., 1982, Atlas of igneous rocks and their textures: New York, N.Y., Wiley, p. 20.	NA
Mineralogical	1987	Dorling, M. and Zussman, J., 1987, Characteristics of asbestiform and non-asbestiform calcic amphiboles: Lithos, v. 20, p. 469-489.	NA
Mineralogical	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA

Table 4. Cleavage

Community	Year	Source	Cleavage
Mineralogical	1993	Klein, C. and Hurlbut, C.S., Jr. ,1993, Manual of mineralogy (after James D. Dana) (21st ed.): New York, N.Y., Wiley, 681 p.	...is the tendency of minerals to break parallel to atomic planes that are identified by Miller indices, just as the faces of the external form of a crystal
Mineralogical	1993	Veblen, D.R. and Wylie, A.G., 1993, Mineralogy of amphiboles and 1:1 layer silicates in Guthrie Jr., G.D. and Mossman, B.T., eds., Health effects of mineral dusts: Reviews in Mineralogy, v. 28, p. 61-137,	Cleavage refers to breakage of a mineral on an approximately planar surface that is controlled by its crystal structure.
Mineralogical	2001	Virta, R.L., 2001, Some facts about asbestos: U.S. Geological Survey Fact Sheet FS-012-01, 4 p.	NA
Mineralogical	2002	http://webmineral.com/help/Fracture.html	If a mineral is strained beyond its elastic limits, it will break. If it breaks irregularly then it shows fracture, if it breaks along regular surfaces related to the crystal structure then it shows cleavage. This cleavage depends on weaknesses in the crystalline make-up of the mineral and is a diagnostic property which can reveal additional information about the mineral.
Mineralogical	2002	http://webmineral.com/help/Habits.html	NA
Regulatory	1974	U.S. District Court, district of Minnesota, 5th Division. Supplemental Memorandum. No. 5-72, Civil 19, Appendix 5, May 11, 1974, p. 24	NA
Regulatory	1976	National Institute for Occupational Safety and Health, 1976, Revised recommended asbestos standard: DHEW (NIOSH) Publication No. 77-169, 96 p.	NA
Regulatory	1983	29 CFR 1910.1001	NA
Regulatory	1990	Ohio Administrative Code (OAC) 3745-20-01	NA
Regulatory	1992	Crane, D., 1992, Polarized light microscopy of asbestos: Occupational Safety and Health Administration Method # ID-191.	NA
Regulatory	1992	Occupational Safety and Health Administration, 1992, Preambles IV. Mineralogical Considerations, National Stone Association and American Mining Congress	NA

Table 4. Cleavage

Community	Year	Source	Cleavage
Regulatory	1993	Perkins, R.L. and Harvey, B.W., 1993, Method for the determination of asbestos in bulk building materials: U.S. Environmental Protection Agency EPA/600/R-93/116, Office of Research and Development, Washington, D.C.	NA
Regulatory	1993	Occupational Safety and Health Administration, 1993, Better protection against asbestos in the workplace: U.S. Department of Labor Fact Sheet No. OSHA 93-06. Available on the world wide web at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FACT_SHEETS&p_id=144	NA
Regulatory	1995	American Society for Testing and Materials, 1995, Standard test method for microvacuum sampling and indirect analysis of dust by transmission electron microscopy for asbestos structure number concentrations: West Conshohocken, Pa., ASTM 5755-95, 13 p.	NA
Regulatory	1995	International Organization for Standardization, 1995, ISO 10312 Ambient air-determination of asbestos fibres-direct-transfer transmission electron microscopy method (1st ed): Geneve, Switzerland, International Organization for Standardization, 51 p.	The breaking of a mineral along one of its crystallographic directions.
Regulatory	1996	Colorado Air Quality Control Commission, 1996, Part B-emission standards for asbestos, *excerpted from* Regulation No. 8 "The control of hazardous air pollutants": Colorado Department of Public Health and Environment, 114 p.	NA
Regulatory	1997	Crane, D., 1997, Asbestos in air: Occupational Safety and Health Administration Method # ID-160.	NA

Table 4. Cleavage

Community	Year	Source	Cleavage
Regulatory	1997	NYCRR (New York Code of Rules & Regulations) Title 10 Section 73.1	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools (7-1-01 Edition)	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools Appendix A (7-1-01 Edition)	NA
Regulatory	2001	29 CFR 1910.1001	NA
Regulatory	2001	30 CFR 56.5001	NA
Regulatory	2001	17 CCR (California Code of Regulations) 93105	NA
Regulatory	2001	West Virginia Code 16-32-2	NA
Regulatory	2002	OAR (Oregon Administrative Rules) 340-248-0010	NA
Regulatory	2002	105 ILCS (Illinois Compiled Statutes Schools) 105/3	NA

Table 5. Cleavage Fragment

Community	Year	Source	Cleavage Fragment
Industrial	1975	Winson, R.W., 1975, Asbestos, *in*, Industrial minerals and rocks (nonmetallics other than fuels): New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 379-425.	NA
Industrial	1981	Steel, E. and Wylie, A., 1981, Mineralogical characteristics of asbestos *in* Riordon, P.H. ed, Geology of Asbestos Deposits, Society of Mining Engineers, p. 93-100.	NA
Industrial	1998	Virta, R.L., 2002, Asbestos: U.S. Geological Survey Open File-Report 02-149, 35 p.	NA
Interdisciplinary	1974	Thompson, C.S., 1974, Discussion of the mineralogy of industrial talcs: U.S. Bureau of Mines Information Circular 8639, p. 22-42.	NA
Interdisciplinary	1978	Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.	NA
Interdisciplinary	1979	Chatfield, E.J., 1979, Measurement of asbestos fibres in the workplace and in the general environment *in* Ledoux, R.L., Mineralogical techniques of asbestos determination: Mineralogical Association of Canada Short Course, v. 4, p. 111-157.	NA
Interdisciplinary	1980	Dixon, W.C., 1980, Applications of optical microscopy in analysis of asbestos and quartz, *chap 2 of* Dollberg, D.D. and Werstuyft, A.W., eds., Analytical techniques in occupational health chemistry: Washington, D.C., American Chemical Society, p. 13-41.	NA
Interdisciplinary	1980	Clark, R.L., 1982, MSHA standard method for fiber identification by electron microscopy: National Bureau of Standards Special Publication 619, p. 207-210.	NA

Table 5. Cleavage Fragment

Community	Year	Source	Cleavage Fragment
Interdisciplinary	1980	Lee, R.J., Kelly, J.F., and Walker, J.S., 1982, Considerations in the analysis and definition of asbestos using electron microscopy: National Bureau of Standards Special Publication 619, p. 132-137.	NA
Interdisciplinary	1980	Chatfield, E.J. and Lewis, G.M., 1980, Development and application of an analytical technique for measurement of asbestos fibers in vermiculite: Scanning Electron Microscopy, p. 329-340.	NA
Interdisciplinary	1984	National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.	...The strength and flexibility of cleavage fragments are approximately the same as those of single crystals. Cleavage cannot produce the high strength and flexibility of asbestiform fibers.
Interdisciplinary	1984	Cossette, M., 1984, Defining asbestos particulates for monitoring purposes *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, p. 5-49.	NA
Interdisciplinary	1984	Ross, M., Kuntze, R.A., and Clifton, R.A., 1984, A definition for asbestos *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, pp.139-147.	NA
Interdisciplinary	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA
Interdisciplinary	1990	Mossman, B.T., Bignon, J., Corn, M., Seaton, A., and Gee, J.B.L., 1990, Asbestos-scientific developments and implications for public policy: Science, v. 247, p. 294-301.	NA
Interdisciplinary	2000	The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2000 by Houghton Mifflin Company.	NA

Table 5. Cleavage Fragment

Community	Year	Source	Cleavage Fragment
Interdisciplinary	2000	Wylie, A.G., 2000, The habit of asbestiform amphiboles: implications for the analysis of bulk samples *in* Beard, M.E. and Rooks, H.L, eds., Advances in environmental measurement methods for asbestos: ASTM Special Technical Publication 1342, p. 53-69.	NA
Interdisciplinary	2001	Beard, M.E., Crankshaw, O.S., Ennis, J.T., and Moore, C.E., 2001, Analysis of crayons for asbestos and other fibrous materials, and recommendations for improved analytical definitions: Research Triangle Park, North Carolina, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, Earth and Mineral Sciences Department, [informal report], 23 p., plus appendices A-H.	Cleavage fragments are mineral particles which are similar to asbestiform fibers but have low aspect ratios.
Interdisciplinary	2001	Nolan, R.P., Langer, A.M., Ross, M., Wicks, F.J., and Martin, R.F., eds., 2001, The health effects of chrysotile asbestos-contribution of science to risk-management decisions: The Canadian Mineralogist Special Publication 5, 304 p.	NA
Medical	1977	Zielhuis, R.L., 1977, Public health risks of exposure to asbestos: Elmsford, N.Y., Pergamon Press Inc., 143 p.	NA
Medical	1979	Langer, A.M., Rohl, A.N., Wolff, M., and Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments-Nomenclature and biological properties, *in* Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.	NA

Table 5. Cleavage Fragment

Community	Year	Source	Cleavage Fragment
Medical	1998	Blake, T., Castranova, V., Schwegler-Berry, D., Baron, P., Deye, G.J., Li, C., and Jones, W., 1998, Effect of fiber length on glass microfiber cytotoxicity: Journal of Toxicology and Environmental Health, v. 54, p. 243-259.	NA
Medical	2001	Ninth Report on Carcinogens, January 2001 http://ehp.niehs.nih.gov/roc/ninth/known/asbestos.pdf	NA
Mineralogical	1914	Dana, E.S., 1914, The system of mineralogy of James Dwight Dana, descriptive mineralogy (6th ed): New York, N.Y., Wiley, p.	NA
Mineralogical	1977	Campbell, W.J., Blake, R.L, Brown, L.L., Cather, E.E., and Sjober, J.J., 1977, Selected silicate minerals and their asbestiform varieties: U.S. Bureau of Mines Information Circular 8751, 56 p.	A fragment produced by the breaking of crystals in directions that are related to the crystal structure and are always parallel to possible crystal faces.
Mineralogical	1979	Campbell, W.J., Steel, E.B., Virta, R.L., and Eisner, M.H., 1979, Relationship of mineral habit to size characteristics for tremolite cleavage fragments and fibers: U.S. Bureau of Mines Report of Investigations 8367, 18 p.	NA
Mineralogical	1980	Bates, R.L., and Jackson, J.A., eds., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.	A fragment of a crystal that is bounded by cleavage faces.
Mineralogical	1982	MacKenzie, W.S., Donaldson, C.H., and Guilford, C., 1982, Atlas of igneous rocks and their textures: New York, N.Y., Wiley, p. 20.	NA
Mineralogical	1987	Dorling, M. and Zussman, J., 1987, Characteristics of asbestiform and non-asbestiform calcic amphiboles: Lithos, v. 20, p. 469-489.	NA
Mineralogical	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA

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Community	Year	Source	Cleavage Fragment
Mineralogical	1993	Klein, C. and Hurlbut, C.S., Jr. ,1993, Manual of mineralogy (after James D. Dana) (21st ed.): New York, N.Y., Wiley, 681 p.	NA
Mineralogical	1993	Veblen, D.R. and Wylie, A.G., 1993, Mineralogy of amphiboles and 1:1 layer silicates in Guthrie Jr., G.D. and Mossman, B.T., eds., Health effects of mineral dusts: Reviews in Mineralogy, v. 28, p. 61-137,	NA
Mineralogical	2001	Virta, R.L., 2001, Some facts about asbestos: U.S. Geological Survey Fact Sheet FS-012-01, 4 p.	NA
Mineralogical	2002	http://webmineral.com/help/Fracture.html	NA
Mineralogical	2002	http://webmineral.com/help/Habits.html	NA
Regulatory	1974	U.S. District Court, district of Minnesota, 5th Division. Supplemental Memorandum. No. 5-72, Civil 19, Appendix 5, May 11, 1974, p. 24	NA
Regulatory	1976	National Institute for Occupational Safety and Health, 1976, Revised recommended asbestos standard: DHEW (NIOSH) Publication No. 77-169, 96 p.	NA
Regulatory	1983	29 CFR 1910.1001	NA
Regulatory	1990	Ohio Administrative Code (OAC) 3745-20-01	NA
Regulatory	1992	Crane, D., 1992, Polarized light microscopy of asbestos: Occupational Safety and Health Administration Method # ID-191.	Mineral particles formed by the comminution of minerals, especially those characterized by relatively parallel sides and moderate aspect ratio.
Regulatory	1992	Occupational Safety and Health Administration, 1992, Preambles IV. Mineralogical Considerations, National Stone Association and American Mining Congress	NA

Table 5. Cleavage Fragment

Community	Year	Source	Cleavage Fragment
Regulatory	1997	Crane, D., 1997, Asbestos in air: Occupational Safety and Health Administration Method # ID-160.	Mineral particles formed by the comminution of minerals, especially those characterized by parallel sides and moderate aspect ratio (usually less than 20:1).
Regulatory	1997	NYCRR (New York Code of Rules & Regulations) Title 10 Section 73.1	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools (7-1-01 Edition)	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools Appendix A (7-1-01 Edition)	NA
Regulatory	2001	29 CFR 1910.1001	NA
Regulatory	2001	30 CFR 56.5001	NA
Regulatory	2001	17 CCR (California Code of Regulations) 93105	NA
Regulatory	2001	West Virginia Code 16-32-2	NA
Regulatory	2002	OAR (Oregon Administrative Rules) 340-248-0010	NA
Regulatory	2002	105 ILCS (Illinois Compiled Statutes Schools) 105/3	NA

Table 6. Fiber

Community	Year	Source	Fiber
Industrial	1975	Winson, R.W., 1975, Asbestos, *in*, Industrial minerals and rocks (nonmetallics other than fuels): New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 379-425.	NA
Industrial	1981	Steel, E. and Wylie, A., 1981, Mineralogical characteristics of asbestos *in* Riordon, P.H. ed, Geology of Asbestos Deposits, Society of Mining Engineers, p. 93-100.	NA
Industrial	1998	Virta, R.L., 2002, Asbestos: U.S. Geological Survey Open File-Report 02-149, 35 p.	NA
Interdisciplinary	1974	Thompson, C.S., 1974, Discussion of the mineralogy of industrial talcs: U.S. Bureau of Mines Information Circular 8639, p. 22-42.	The term "fiber" connotes a greatly elongated particle with threadlike qualities such as high-tensile strength, flexibility, spinability, etc.
Interdisciplinary	1978	Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.	An acicular single crystal, or a similarly elongated polycrystalline aggregate, which displays some resemblance to organic fibers.
Interdisciplinary	1979	Chatfield, E.J., 1979, Measurement of asbestos fibres in the workplace and in the general environment *in* Ledoux, R.L., Mineralogical techniques of asbestos determination: Mineralogical Association of Canada Short Course, v. 4, p. 111-157.	
Interdisciplinary	1980	Dixon, W.C., 1980, Applications of optical microscopy in analysis of asbestos and quartz, *chap 2 of* Dollberg, D.D. and Werstuyft, A.W., eds., Analytical techniques in occupational health chemistry: Washington, D.C., American Chemical Society, p. 13-41.	NA
Interdisciplinary	1980	Clark, R.L., 1982, MSHA standard method for fiber identification by electron microscopy: National Bureau of Standards Special Publication 619, p. 207-210.	[*Author uses Code of Federal Regulations*] "fiber" is defined as any particulate with a three to one or greater length to width aspect ratio, and a length of five micrometers or longer.

Table 6. Fiber

Community	Year	Source	Fiber
Interdisciplinary	1980	Lee, R.J., Kelly, J.F., and Walker, J.S., 1982, Considerations in the analysis and definition of asbestos using electron microscopy: National Bureau of Standards Special Publication 619, p. 132-137.	NA
Interdisciplinary	1980	Chatfield, E.J. and Lewis, G.M., 1980, Development and application of an analytical technique for measurement of asbestos fibers in vermiculite: Scanning Electron Microscopy, p. 329-340.	Fibers are defined as all fragments having aspect ratios greater than 3:1, with lengths exceeding 5 um and having diameters smaller than 3 um.
Interdisciplinary	1984	National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.	The term MINERAL FIBERS has traditionally referred to crystals whose appearance and properties resembled organic fibers, such as hair and cotton. In some recent literature, however, the term sometimes refers only to the appearance of the material, and there can be confusion about whether particular properties are also implied.
Interdisciplinary	1984	Cossette, M., 1984, Defining asbestos particulates for monitoring purposes in Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, p. 5-49.	NA
Interdisciplinary	1984	Ross, M., Kuntze, R.A., and Clifton, R.A., 1984, A definition for asbestos in Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, pp.139-147.	NA
Interdisciplinary	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	...inorganic fibers in a general sense: as small elongate solid objects composed of any compound or element; usually nonbiologic in origin and often exhibiting distinctive physical, especially mechanical, properties. Inorganic fibers can occur naturally, that is, as mineral fibers or can be produced synthetically.
Interdisciplinary	1990	Mossman, B.T., Bignon, J., Corn, M., Seaton, A., and Gee, J.B.L., 1990, Asbestos-scientific developments and implications for public policy: Science, v. 247, p. 294-301.	NA

Table 6. Fiber

Community	Year	Source	Fiber
Interdisciplinary	2000	The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2000 by Houghton Mifflin Company.	NA
Interdisciplinary	2000	Wylie, A.G., 2000, The habit of asbestiform amphiboles: implications for the analysis of bulk samples in Beard, M.E. and Rooks, H.L, eds., Advances in environmental measurement methods for asbestos: ASTM Special Technical Publication 1342, p. 53-69.	NA
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Medical	1977	Zielhuis, R.L., 1977, Public health risks of exposure to asbestos: Elmsford, N.Y., Pergamon Press Inc., 143 p.	NA
Medical	1979	Langer, A.M., Rohl, A.N., Wolff, M., and Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments-Nomenclature and biological properties, in Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.	NA

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Community	Year	Source	Fiber
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Medical	2001	Ninth Report on Carcinogens, January 2001 http://ehp.niehs.nih.gov/roc/nint h/known/asbestos.pdf	NA
Mineralogical	1914	Dana, E.S., 1914, The system of mineralogy of James Dwight Dana, descriptive mineralogy (6th ed): New York, N.Y., Wiley, p.	NA
Mineralogical	1977	Campbell, W.J., Blake, R.L, Brown, L.L., Cather, E.E., and Sjober, J.J., 1977, Selected silicate minerals and their asbestiform varieties: U.S. Bureau of Mines Information Circular 8751, 56 p.	(mineral fiber) The smallest elongated crystalline unit that can be separated from a bundle or appears to have grown individually in that shape, and that exhibits a resemblance to organic fibers. (Examples: fiber bundles, chrysotile, and crocidolite; individual fibers, epsomite and millerite.)
Mineralogical	1979	Campbell, W.J., Steel, E.B., Virta, R.L., and Eisner, M.H., 1979, Relationship of mineral habit to size characteristics for tremolite cleavage fragments and fibers: U.S. Bureau of Mines Report of Investigations 8367, 18 p.	NA
Mineralogical	1980	Bates, R.L., and Jackson, J.A., eds., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.	An elongated, tapering, thick-walled strengthening cell occurring in various parts of vascular plants (Esau, 1953).
Mineralogical	1982	MacKenzie, W.S., Donaldson, C.H., and Guilford, C., 1982, Atlas of igneous rocks and their textures: New York, N.Y., Wiley, p. 20.	NA
Mineralogical	1987	Dorling, M. and Zussman, J., 1987, Characteristics of asbestiform and non-asbestiform calcic amphiboles: Lithos, v. 20, p. 469-489.	NA

Table 6. Fiber

Community	Year	Source	Fiber
Mineralogical	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	A long, thin thread or threadlike solid with distinctive elongate shape that may be natural or synthetic and organic or inorganic in composition. The properties of flexibility and toughness are also implied, especially to the layperson, but are not essential to the definition. The dimensions of an object called a fiber are usually unspecified and may range from the visible (diameter about a millimeter, and a length many times the thickness) to a particle that can be observed only with the aid of a light or an electron microscope (magnification greater than X50,000). The physical dimensions of vegetable fibers such as flax, hemp, or cotton; animal fibers such as wood, silk, and hair; mineral fibers, such as asbestos; and synthetic fibers such as nylon and glass usually have diameters between 1 and 500 micrometers and lengths between 10 and 1000 micrometers. Inorganic fibers may be flexible and elastic or stiff and brittle, and they commonly occur as aggregates or fibrous bundles. Most mineralogists apply the term when the aspect ratio of a mineral sample, individual or aggregate, is at least 10.
Mineralogical	1993	Klein, C. and Hurlbut, C.S., Jr. ,1993, Manual of mineralogy (after James D. Dana) (21st ed.): New York, N.Y., Wiley, 681 p.	NA
Mineralogical	1993	Veblen, D.R. and Wylie, A.G., 1993, Mineralogy of amphiboles and 1:1 layer silicates in Guthrie Jr., G.D. and Mossman, B.T., eds., Health effects of mineral dusts: Reviews in Mineralogy, v. 28, p. 61-137,	NA
Mineralogical	2001	Virta, R.L., 2001, Some facts about asbestos: U.S. Geological Survey Fact Sheet FS-012-01, 4 p.	NA
Mineralogical	2002	http://webmineral.com/help/Fracture.html	NA
Mineralogical	2002	http://webmineral.com/help/Habits.html	NA
Regulatory	1974	U.S. District Court, district of Minnesota, 5th Division. Supplemental Memorandum. No. 5-72, Civil 19, Appendix 5, May 11, 1974, p. 24	...a mineral which is at least three times as long as it is wide

Table 6. Fiber

Community	Year	Source	Fiber
Regulatory	1976	National Institute for Occupational Safety and Health, 1976, Revised recommended asbestos standard: DHEW (NIOSH) Publication No. 77-169, 96 p.	Asbestos fibers are defined as those particles with a length greater than 5 um and a length-to-diameter ratio of 3:1, or greater.
Regulatory	1983	29 CFR 1910.1001	(2) "Asbestos fibers" means asbestos fibers longer than 5 micrometers.
Regulatory	1990	Ohio Administrative Code (OAC) 3745-20-01	NA
Regulatory	1992	Crane, D., 1992, Polarized light microscopy of asbestos: Occupational Safety and Health Administration Method # ID-191.	A particle longer than or equal to 5 um with a length to width ratio greater than or equal to 3:1. This may include cleavage fragments.
Regulatory	1992	Occupational Safety and Health Administration, 1992, Preambles IV. Mineralogical Considerations, National Stone Association and American Mining Congress	NA
Regulatory	1993	Perkins, R.L. and Harvey, B.W., 1993, Method for the determination of asbestos in bulk building materials: U.S. Environmental Protection Agency EPA/600/R-93/116, Office of Research and Development, Washington, D.C.	With reference to asbestiform morphology, a structure consisting of one or more fibrils.
Regulatory	1993	Occupational Safety and Health Administration, 1993, Better protection against asbestos in the workplace: U.S. Department of Labor Fact Sheet No. OSHA 93-06. Available on the world wide web at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FACT_SHEETS&p_id=144	NA
Regulatory	1995	American Society for Testing and Materials, 1995, Standard test method for microvacuum sampling and indirect analysis of dust by transmission electron microscopy for asbestos structure number concentrations: West Conshohocken, Pa., ASTM 5755-95, 13 p.	a structure having a minimum length of 0.5 um, an aspect ratio of 5:1 or greater, and substantially parallel sides

Table 6. Fiber

Community	Year	Source	Fiber
Regulatory	1995	International Organization for Standardization, 1995, ISO 10312 Ambient air-determination of asbestos fibres-direct-transfer transmission electron microscopy method (1st ed): Geneve, Switzerland, International Organization for Standardization, 51 p.	(fibre) An elongated particle which has parallel or stepped sides. For the purposes of this International Standard, a fibre is defined to have an aspect ratio equal to or greater than 5:1 and a minimum length of 0.5 um.
Regulatory	1996	Colorado Air Quality Control Commission, 1996, Part B-emission standards for asbestos, *excerpted from* Regulation No. 8 "The control of hazardous air pollutants": Colorado Department of Public Health and Environment, 114 p.	NA
Regulatory	1997	Crane, D., 1997, Asbestos in air: Occupational Safety and Health Administration Method # ID-160.	A particle that is 5 um or longer, with a length-to-width ratio of 3 to 1 or longer.
Regulatory	1997	NYCRR (New York Code of Rules & Regulations) Title 10 Section 73.1	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools (7-1-01 Edition)	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools Appendix A (7-1-01 Edition)	A structure greater than or equal to 0.5 um in length with an aspect ratio (length to width) of 5:1 or greater and having substantially parallel sides.
Regulatory	2001	29 CFR 1910.1001	Fiber means a particulate form of asbestos 5 micrometers or longer, with a length-to-diameter ratio of at least 3 to 1.
Regulatory	2001	30 CFR 56.5001	NA
Regulatory	2001	17 CCR (California Code of Regulations) 93105	NA
Regulatory	2001	West Virginia Code 16-32-2	NA
Regulatory	2002	OAR (Oregon Administrative Rules) 340-248-0010	NA
Regulatory	2002	105 ILCS (Illinois Compiled Statutes Schools) 105/3	NA

Table 7. Fibril

Community	Year	Source	Fibril
Industrial	1975	Winson, R.W., 1975, Asbestos, *in*, Industrial minerals and rocks (nonmetallics other than fuels): New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 379-425.	NA
Industrial	1981	Steel, E. and Wylie, A., 1981, Mineralogical characteristics of asbestos *in* Riordon, P.H. ed, Geology of Asbestos Deposits, Society of Mining Engineers, p. 93-100.	A fibril is single or twinned crystal with a very small width, generally less than 0.5 um, and an extremely high aspect ratio; bundle of fibrils may have lengths reaching into the cm.
Industrial	1998	Virta, R.L., 2002, Asbestos: U.S. Geological Survey Open File-Report 02-149, 35 p.	NA
Interdisciplinary	1974	Thompson, C.S., 1974, Discussion of the mineralogy of industrial talcs: U.S. Bureau of Mines Information Circular 8639, p. 22-42.	NA
Interdisciplinary	1978	Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.	NA
Interdisciplinary	1979	Chatfield, E.J., 1979, Measurement of asbestos fibres in the workplace and in the general environment *in* Ledoux, R.L., Mineralogical techniques of asbestos determination: Mineralogical Association of Canada Short Course, v. 4, p. 111-157.	NA
Interdisciplinary	1980	Dixon, W.C., 1980, Applications of optical microscopy in analysis of asbestos and quartz, *chap 2 of* Dollberg, D.D. and Werstuyft, A.W., eds., Analytical techniques in occupational health chemistry: Washington, D.C., American Chemical Society, p. 13-41.	NA

Table 7. Fibril

Community	Year	Source	Fibril
Interdisciplinary	1980	Clark, R.L., 1982, MSHA standard method for fiber identification by electron microscopy: National Bureau of Standards Special Publication 619, p. 207-210.	NA
Interdisciplinary	1980	Lee, R.J., Kelly, J.F., and Walker, J.S., 1982, Considerations in the analysis and definition of asbestos using electron microscopy: National Bureau of Standards Special Publication 619, p. 132-137.	NA
Interdisciplinary	1980	Chatfield, E.J. and Lewis, G.M., 1980, Development and application of an analytical technique for measurement of asbestos fibers in vermiculite: Scanning Electron Microscopy, p. 329-340.	NA
Interdisciplinary	1984	National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.	NA
Interdisciplinary	1984	Cossette, M., 1984, Defining asbestos particulates for monitoring purposes in Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, p. 5-49.	...a single crystal in the form of a fiber
Interdisciplinary	1984	Ross, M., Kuntze, R.A., and Clifton, R.A., 1984, A definition for asbestos in Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, pp.139-147.	NA

Table 7. Fibril

Community	Year	Source	Fibril
Interdisciplinary	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	A small fiber or the subdivision of a fiber (OED); also a small thread or fiber (WEB). The term is usually employed to describe an elongate unit whose dimensions are smaller than fiber (fine-fibrous) and may be used to designate one member of a fibrous mineral aggregate, regardless of the size of the individual particles or the aggregate. In the latter usage, the implication is that a fibril is the smallest unit that expresses the characteristics of a fiber or fibrous mass, and usually that the fibril is separable by subdivision parallel to the length of the fiber. For example, chrysotile asbestos could theoretically be disaggregated to tubular individual fibrils with diameters in the range of 200 A. The term fibril therefore has an ultimate lower limit. Fibril is also related to the term polymer, which is defined as a chemical compound or mixture of compounds formed by polymerization and consisting of essentially repeating structural units, usually producing giant chainlike macromolecules. Such a molecule is characterized by highly asymmetric geometry and anisotropic properties. If a solid is formed from polymers, a fibril would be the smallest polymeric unit.
Interdisciplinary	1990	Mossman, B.T., Bignon, J., Corn, M., Seaton, A., and Gee, J.B.L., 1990, Asbestos-scientific developments and implications for public policy: Science, v. 247, p. 294-301.	NA
Interdisciplinary	2000	The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2000 by Houghton Mifflin Company.	1. A small slender fiber or filament
Interdisciplinary	2000	Wylie, A.G., 2000, The habit of asbestiform amphiboles: implications for the analysis of bulk samples in Beard, M.E. and Rooks, H.L, eds., Advances in environmental measurement methods for asbestos: ASTM Special Technical Publication 1342, p. 53-69.	NA

Table 7. Fibril

Community	Year	Source	Fibril
Interdisciplinary	2001	Beard, M.E., Crankshaw, O.S., Ennis, J.T., and Moore, C.E., 2001, Analysis of crayons for asbestos and other fibrous materials, and recommendations for improved analytical definitions: Research Triangle Park, North Carolina, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, Earth and Mineral Sciences Department, [informal report], 23 p., plus appendices A-H.	NA
Interdisciplinary	2001	Nolan, R.P., Langer, A.M., Ross, M., Wicks, F.J., and Martin, R.F., eds., 2001, The health effects of chrysotile asbestos-contribution of science to risk-management decisions: The Canadian Mineralogist Special Publication 5, 304 p.	NA
Medical	1977	Zielhuis, R.L., 1977, Public health risks of exposure to asbestos: Elmsford, N.Y., Pergamon Press Inc., 143 p.	Chrysotile having a high magnesium content can be described as a sheet silicate in which the flat structure is rolled about an axis to form a narrow tube (termed fibril) possessing both strength and flexibility.
Medical	1979	Langer, A.M., Rohl, A.N., Wolff, M., and Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments-Nomenclature and biological properties, in Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.	NA
Medical	1998	Blake, T., Castranova, V., Schwegler-Berry, D., Baron, P., Deye, G.J., Li, C., and Jones, W., 1998, Effect of fiber length on glass microfiber cytotoxicity: Journal of Toxicology and Environmental Health, v. 54, p. 243-259.	NA
Medical	2001	Ninth Report on Carcinogens, January 2001 http://ehp.niehs.nih.gov/roc/ninth/known/asbestos.pdf	NA

Table 7. Fibril

Community	Year	Source	Fibril
Mineralogical	1914	Dana, E.S., 1914, The system of mineralogy of James Dwight Dana, descriptive mineralogy (6th ed): New York, N.Y., Wiley, p.	NA
Mineralogical	1977	Campbell, W.J., Blake, R.L, Brown, L.L., Cather, E.E., and Sjober, J.J., 1977, Selected silicate minerals and their asbestiform varieties: U.S. Bureau of Mines Information Circular 8751, 56 p.	A single fiber, which cannot be separated into smaller components without losing its fibrous properties or appearances.
Mineralogical	1979	Campbell, W.J., Steel, E.B., Virta, R.L., and Eisner, M.H., 1979, Relationship of mineral habit to size characteristics for tremolite cleavage fragments and fibers: U.S. Bureau of Mines Report of Investigations 8367, 18 p.	NA
Mineralogical	1980	Bates, R.L., and Jackson, J.A., eds., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.	NA
Mineralogical	1982	MacKenzie, W.S., Donaldson, C.H., and Guilford, C., 1982, Atlas of igneous rocks and their textures: New York, N.Y., Wiley, p. 20.	NA
Mineralogical	1987	Dorling, M. and Zussman, J., 1987, Characteristics of asbestiform and non-asbestiform calcic amphiboles: Lithos, v. 20, p. 469-489.	NA
Mineralogical	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA
Mineralogical	1993	Klein, C. and Hurlbut, C.S., Jr. ,1993, Manual of mineralogy (after James D. Dana) (21st ed.): New York, N.Y., Wiley, 681 p.	NA

Table 7. Fibril

Community	Year	Source	Fibril
Mineralogical	1993	Veblen, D.R. and Wylie, A.G., 1993, Mineralogy of amphiboles and 1:1 layer silicates in Guthrie Jr., G.D. and Mossman, B.T., eds., Health effects of mineral dusts: Reviews in Mineralogy, v. 28, p. 61-137,	Fibrils are single, elementary fibers that have very small width.
Mineralogical	2001	Virta, R.L., 2001, Some facts about asbestos: U.S. Geological Survey Fact Sheet FS-012-01, 4 p.	NA
Mineralogical	2002	http://webmineral.com/help/Fracture.html	NA
Mineralogical	2002	http://webmineral.com/help/Habits.html	NA
Regulatory	1974	U.S. District Court, district of Minnesota, 5th Division. Supplemental Memorandum. No. 5-72, Civil 19, Appendix 5, May 11, 1974, p. 24	NA
Regulatory	1976	National Institute for Occupational Safety and Health, 1976, Revised recommended asbestos standard: DHEW (NIOSH) Publication No. 77-169, 96 p.	NA
Regulatory	1983	29 CFR 1910.1001	NA
Regulatory	1990	Ohio Administrative Code (OAC) 3745-20-01	NA
Regulatory	1992	Crane, D., 1992, Polarized light microscopy of asbestos: Occupational Safety and Health Administration Method # ID-191.	NA
Regulatory	1992	Occupational Safety and Health Administration, 1992, Preambles IV. Mineralogical Considerations, National Stone Association and American Mining Congress	NA
Regulatory	1993	Perkins, R.L. and Harvey, B.W., 1993, Method for the determination of asbestos in bulk building materials: U.S. Environmental Protection Agency EPA/600/R-93/116, Office of Research and Development, Washington, D.C.	The individual unit of structure of fibers.

Table 7. Fibril

Community	Year	Source	Fibril
Regulatory	1993	Occupational Safety and Health Administration, 1993, Better protection against asbestos in the workplace: U.S. Department of Labor Fact Sheet No. OSHA 93-06. Available on the world wide web at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FACT_SHEETS&p_id=144	NA
Regulatory	1995	American Society for Testing and Materials, 1995, Standard test method for microvacuum sampling and indirect analysis of dust by transmission electron microscopy for asbestos structure number concentrations: West Conshohocken, Pa., ASTM 5755-95, 13 p.	a single fiber that cannot be separated into smaller components without losing its fibrous properties or appearance.
Regulatory	1995	International Organization for Standardization, 1995, ISO 10312 Ambient air-determination of asbestos fibres-direct-transfer transmission electron microscopy method (1st ed): Geneve, Switzerland, International Organization for Standardization, 51 p.	A single fibre of asbestos, which cannot be further separated longitudinally into smaller components without losing its fibrous properties or appearances.
Regulatory	1996	Colorado Air Quality Control Commission, 1996, Part B-emission standards for asbestos, *excerpted from* Regulation No. 8 "The control of hazardous air pollutants": Colorado Department of Public Health and Environment, 114 p.	NA
Regulatory	1997	Crane, D., 1997, Asbestos in air: Occupational Safety and Health Administration Method # ID-160.	NA
Regulatory	1997	NYCRR (New York Code of Rules & Regulations) Title 10 Section 73.1	NA

Table 7. Fibril

Community	Year	Source	Fibril
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools (7-1-01 Edition)	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools Appendix A (7-1-01 Edition)	NA
Regulatory	2001	29 CFR 1910.1001	NA
Regulatory	2001	30 CFR 56.5001	NA
Regulatory	2001	17 CCR (California Code of Regulations) 93105	NA
Regulatory	2001	West Virginia Code 16-32-2	NA
Regulatory	2002	OAR (Oregon Administrative Rules) 340-248-0010	NA
Regulatory	2002	105 ILCS (Illinois Compiled Statutes Schools) 105/3	NA

Table 8. Fibrous

Community	Year	Source	Fibrous
Industrial	1975	Winson, R.W., 1975, Asbestos, *in*, Industrial minerals and rocks (nonmetallics other than fuels): New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 379-425.	NA
Industrial	1981	Steel, E. and Wylie, A., 1981, Mineralogical characteristics of asbestos *in* Riordon, P.H. ed, Geology of Asbestos Deposits, Society of Mining Engineers, p. 93-100.	NA
Industrial	1998	Virta, R.L., 2002, Asbestos: U.S. Geological Survey Open File-Report 02-149, 35 p.	NA
Interdisciplinary	1974	Thompson, C.S., 1974, Discussion of the mineralogy of industrial talcs: U.S. Bureau of Mines Information Circular 8639, p. 22-42.	NA
Interdisciplinary	1978	Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.	The descriptive term used for a mineral which is composed of parallel, radiating or interlaced aggregates of fibers, from which the fibers are usually separable.
Interdisciplinary	1979	Chatfield, E.J., 1979, Measurement of asbestos fibres in the workplace and in the general environment *in* Ledoux, R.L., Mineralogical techniques of asbestos determination: Mineralogical Association of Canada Short Course, v. 4, p. 111-157.	NA
Interdisciplinary	1980	Dixon, W.C., 1980, Applications of optical microscopy in analysis of asbestos and quartz, *chap 2 of* Dollberg, D.D. and Werstuyft, A.W., eds., Analytical techniques in occupational health chemistry: Washington, D.C., American Chemical Society, p. 13-41.	NA

Table 8. Fibrous

Community	Year	Source	Fibrous
Interdisciplinary	1980	Clark, R.L., 1982, MSHA standard method for fiber identification by electron microscopy: National Bureau of Standards Special Publication 619, p. 207-210.	NA
Interdisciplinary	1980	Lee, R.J., Kelly, J.F., and Walker, J.S., 1982, Considerations in the analysis and definition of asbestos using electron microscopy: National Bureau of Standards Special Publication 619, p. 132-137.	NA
Interdisciplinary	1980	Chatfield, E.J. and Lewis, G.M., 1980, Development and application of an analytical technique for measurement of asbestos fibers in vermiculite: Scanning Electron Microscopy, p. 329-340.	NA
Interdisciplinary	1984	National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.	FIBROUS refers to (1) single crystals that resemble organic fibers such as hair or cotton and (2) large crystals or crystalline aggregates that look like they are composed of fibers (I.e., long, thin, needlelike elements) (Dana and Ford, 1932). The apparent fibers do not need to be separable. If the fibers are separable and are strong and flexible, they are ASBESTIFORM. If they have the normal strength and brittleness of the mineral, they are ACICULAR. If the apparent fibers are not separable, the specimen may be a single crystal or a multiple (polycrystalline) aggregate displaying a fibrous pattern (resulting, for example, from striation or pseudomorphic replacement of an initially fibrous mineral).
Interdisciplinary	1984	Cossette, M., 1984, Defining asbestos particulates for monitoring purposes in Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, p. 5-49.	fibrous particulate-fibers, fiber fragments, and fiber agglomerates
Interdisciplinary	1984	Ross, M., Kuntze, R.A., and Clifton, R.A., 1984, A definition for asbestos in Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, pp.139-147.	NA

Table 8. Fibrous

Community	Year	Source	Fibrous
Interdisciplinary	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	Full of fibers, or formed of fibers (OED), with dimensions unspecified but implied, by comparison, to be similar to the natural materials thread and hair (see Fiber). Aggregates of any size of individual fibers may form relatively thick fibrous bundles, thus becoming visible to the naked eye.
Interdisciplinary	1990	Mossman, B.T., Bignon, J., Corn, M., Seaton, A., and Gee, J.B.L., 1990, Asbestos-scientific developments and implications for public policy: Science, v. 247, p. 294-301.	NA
Interdisciplinary	2000	The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2000 by Houghton Mifflin Company.	1. Having, consisting of, or resembling fibers.
Interdisciplinary	2000	Wylie, A.G., 2000, The habit of asbestiform amphiboles: implications for the analysis of bulk samples *in* Beard, M.E. and Rooks, H.L, eds., Advances in environmental measurement methods for asbestos: ASTM Special Technical Publication 1342, p. 53-69.	NA
Interdisciplinary	2001	Beard, M.E., Crankshaw, O.S., Ennis, J.T., and Moore, C.E., 2001, Analysis of crayons for asbestos and other fibrous materials, and recommendations for improved analytical definitions: Research Triangle Park, North Carolina, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, Earth and Mineral Sciences Department, [informal report], 23 p., plus appendices A-H.	NA
Interdisciplinary	2001	Nolan, R.P., Langer, A.M., Ross, M., Wicks, F.J., and Martin, R.F., eds., 2001, The health effects of chrysotile asbestos-contribution of science to risk-management decisions: The Canadian Mineralogist Special Publication 5, 304 p.	NA

Table 8. Fibrous

Community	Year	Source	Fibrous
Medical	1977	Zielhuis, R.L., 1977, Public health risks of exposure to asbestos: Elmsford, N.Y., Pergamon Press Inc., 143 p.	NA
Medical	1979	Langer, A.M., Rohl, A.N., Wolff, M., and Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments- Nomenclature and biological properties, *in* Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.	NA
Medical	1998	Blake, T., Castranova, V., Schwegler-Berry, D., Baron, P., Deye, G.J., Li, C., and Jones, W., 1998, Effect of fiber length on glass microfiber cytotoxicity: Journal of Toxicology and Environmental Health, v. 54, p. 243-259.	NA
Medical	2001	Ninth Report on Carcinogens, January 2001 http://ehp.niehs.nih.gov/roc/ninth/known/asbestos.pdf	NA
Mineralogical	1914	Dana, E.S., 1914, The system of mineralogy of James Dwight Dana, descriptive mineralogy (6th ed): New York, N.Y., Wiley, p.	NA
Mineralogical	1977	Campbell, W.J., Blake, R.L, Brown, L.L., Cather, E.E., and Sjober, J.J., 1977, Selected silicate minerals and their asbestiform varieties: U.S. Bureau of Mines Information Circular 8751, 56 p.	The occurrence of a mineral in bundles of fibers, resembling organic fibers in texture, from which the fibers can usually be separated (for example, satin-spar and chrysotile).
Mineralogical	1979	Campbell, W.J., Steel, E.B., Virta, R.L., and Eisner, M.H., 1979, Relationship of mineral habit to size characteristics for tremolite cleavage fragments and fibers: U.S. Bureau of Mines Report of Investigations 8367, 18 p.	The term fibrous is used in a general mineralogical way to describe any aggregates of grains that crystallize in a needlelike habit and appear to be composed of fibers.
Mineralogical	1980	Bates, R.L., and Jackson, J.A., eds., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.	Said of the habit of a mineral, and of the mineral itself (e.g. asbestos), that crystallizes in elongated thin, needle-like grains, or fibers.

Table 8. Fibrous

Community	Year	Source	Fibrous
Mineralogical	1982	MacKenzie, W.S., Donaldson, C.H., and Guilford, C., 1982, Atlas of igneous rocks and their textures: New York, N.Y., Wiley, p. 20.	NA
Mineralogical	1987	Dorling, M. and Zussman, J., 1987, Characteristics of asbestiform and non-asbestiform calcic amphiboles: Lithos, v. 20, p. 469-489.	NA
Mineralogical	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA
Mineralogical	1993	Klein, C. and Hurlbut, C.S., Jr. ,1993, Manual of mineralogy (after James D. Dana) (21st ed.): New York, N.Y., Wiley, 681 p.	Aggregate of slender fibers, parallel or radiating
Mineralogical	1993	Veblen, D.R. and Wylie, A.G., 1993, Mineralogy of amphiboles and 1:1 layer silicates in Guthrie Jr., G.D. and Mossman, B.T., eds., Health effects of mineral dusts: Reviews in Mineralogy, v. 28, p. 61-137,	NA
Mineralogical	2001	Virta, R.L., 2001, Some facts about asbestos: U.S. Geological Survey Fact Sheet FS-012-01, 4 p.	When the length is extremely long compared with the width, the crystals are called asbestiform or fibrous.
Mineralogical	2002	http://webmineral.com/help/Fracture.html	[About fibrous fracture] Thin, elongated fractures produced by crystal forms or intersecting cleavages (e.g. asbestos).
Mineralogical	2002	http://webmineral.com/help/Habits.html	[About mineral habit] Crystals made up of fibers.
Regulatory	1974	U.S. District Court, district of Minnesota, 5th Division. Supplemental Memorandum. No. 5-72, Civil 19, Appendix 5, May 11, 1974, p. 24	NA
Regulatory	1976	National Institute for Occupational Safety and Health, 1976, Revised recommended asbestos standard: DHEW (NIOSH) Publication No. 77-169, 96 p.	NA
Regulatory	1983	29 CFR 1910.1001	NA
Regulatory	1990	Ohio Administrative Code (OAC) 3745-20-01	NA

Table 8. Fibrous

Community	Year	Source	Fibrous
Regulatory	1992	Crane, D., 1992, Polarized light microscopy of asbestos: Occupational Safety and Health Administration Method # ID-191.	NA
Regulatory	1992	Occupational Safety and Health Administration, 1992, Preambles IV. Mineralogical Considerations, National Stone Association and American Mining Congress	NA
Regulatory	1993	Perkins, R.L. and Harvey, B.W., 1993, Method for the determination of asbestos in bulk building materials: U.S. Environmental Protection Agency EPA/600/R-93/116, Office of Research and Development, Washington, D.C.	NA
Regulatory	1993	Occupational Safety and Health Administration, 1993, Better protection against asbestos in the workplace: U.S. Department of Labor Fact Sheet No. OSHA 93-06. Available on the world wide web at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FACT_SHEETS&p_id=144	NA
Regulatory	1995	American Society for Testing and Materials, 1995, Standard test method for microvacuum sampling and indirect analysis of dust by transmission electron microscopy for asbestos structure number concentrations: West Conshohocken, Pa., ASTM 5755-95, 13 p.	...of a mineral composed of parallel, radiating, or interlaced aggregates of fibers, from which the fibers are sometimes separable. That is, the crystalline aggregate may be referred to as fibrous even if it is not composed of separable fibers, but has that distinct appearance. The term fibrous is used in a general mineralogical way to describe aggregates of grains that crystallize in a needle-like habit and appear to be composed of fibers. Fibrous has a much more general meaning than asbestos. While it is correct that all asbestos minerals are fibrous, not all minerals having fibrous habits are asbestos.

Table 8. Fibrous

Community	Year	Source	Fibrous
Regulatory	1995	International Organization for Standardization, 1995, ISO 10312 Ambient air-determination of asbestos fibres-direct-transfer transmission electron microscopy method (1st ed): Geneve, Switzerland, International Organization for Standardization, 51 p.	(fibrous structure) A fibre, or connected grouping of fibres, with or without other particles.
Regulatory	1996	Colorado Air Quality Control Commission, 1996, Part B-emission standards for asbestos, *excerpted from* Regulation No. 8 "The control of hazardous air pollutants": Colorado Department of Public Health and Environment, 114 p.	NA
Regulatory	1997	Crane, D., 1997, Asbestos in air: Occupational Safety and Health Administration Method # ID-160.	NA
Regulatory	1997	NYCRR (New York Code of Rules & Regulations) Title 10 Section 73.1	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools (7-1-01 Edition)	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools Appendix A (7-1-01 Edition)	NA
Regulatory	2001	29 CFR 1910.1001	NA
Regulatory	2001	30 CFR 56.5001	NA
Regulatory	2001	17 CCR (California Code of Regulations) 93105	NA
Regulatory	2001	West Virginia Code 16-32-2	NA
Regulatory	2002	OAR (Oregon Administrative Rules) 340-248-0010	NA
Regulatory	2002	105 ILCS (Illinois Compiled Statutes Schools) 105/3	NA

Table 9. Parting

Community	Year	Source	Parting
Industrial	1975	Winson, R.W., 1975, Asbestos, *in*, Industrial minerals and rocks (nonmetallics other than fuels): New York, N.Y., American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 379-425.	NA
Industrial	1981	Steel, E. and Wylie, A., 1981, Mineralogical characteristics of asbestos *in* Riordon, P.H. ed, Geology of Asbestos Deposits, Society of Mining Engineers, p. 93-100.	NA
Industrial	1998	Virta, R.L., 2002, Asbestos: U.S. Geological Survey Open File-Report 02-149, 35 p.	NA
Interdisciplinary	1974	Thompson, C.S., 1974, Discussion of the mineralogy of industrial talcs: U.S. Bureau of Mines Information Circular 8639, p. 22-42.	NA
Interdisciplinary	1978	Zoltai, Tibor, 1978, History of asbestos-related mineralogical terminology: National Bureau of Standards Special Publication 506, p. 1-18.	NA
Interdisciplinary	1979	Chatfield, E.J., 1979, Measurement of asbestos fibres in the workplace and in the general environment *in* Ledoux, R.L., Mineralogical techniques of asbestos determination: Mineralogical Association of Canada Short Course, v. 4, p. 111-157.	NA
Interdisciplinary	1980	Dixon, W.C., 1980, Applications of optical microscopy in analysis of asbestos and quartz, *chap 2 of* Dollberg, D.D. and Werstuyft, A.W., eds., Analytical techniques in occupational health chemistry: Washington, D.C., American Chemical Society, p. 13-41.	When a mineral breaks along a plane of structural weakness it exhibits parting.
Interdisciplinary	1980	Clark, R.L., 1982, MSHA standard method for fiber identification by electron microscopy: National Bureau of Standards Special Publication 619, p. 207-210.	NA

Table 9. Parting

Community	Year	Source	Parting
Interdisciplinary	1980	Lee, R.J., Kelly, J.F., and Walker, J.S., 1982, Considerations in the analysis and definition of asbestos using electron microscopy: National Bureau of Standards Special Publication 619, p. 132-137.	NA
Interdisciplinary	1980	Chatfield, E.J. and Lewis, G.M., 1980, Development and application of an analytical technique for measurement of asbestos fibers in vermiculite: Scanning Electron Microscopy, p. 329-340.	NA
Interdisciplinary	1984	National Research Council, 1984, Asbestiform fibers-nonoccupational health risks: Washington D.C., National Academy Press, p. 25-47.	NA
Interdisciplinary	1984	Cossette, M., 1984, Defining asbestos particulates for monitoring purposes *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, p. 5-49.	NA
Interdisciplinary	1984	Ross, M., Kuntze, R.A., and Clifton, R.A., 1984, A definition for asbestos *in* Levadie, B. ed., Definitions for asbestos and other health-related silicates: ASTM Special Technical Publication 834, pp.139-147.	NA
Interdisciplinary	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA
Interdisciplinary	1990	Mossman, B.T., Bignon, J., Corn, M., Seaton, A., and Gee, J.B.L., 1990, Asbestos-scientific developments and implications for public policy: Science, v. 247, p. 294-301.	NA
Interdisciplinary	2000	The American Heritage® Dictionary of the English Language, Fourth Edition Copyright © 2000 by Houghton Mifflin Company.	NA

Table 9. Parting

Community	Year	Source	Parting
Interdisciplinary	2000	Wylie, A.G., 2000, The habit of asbestiform amphiboles: implications for the analysis of bulk samples *in* Beard, M.E. and Rooks, H.L, eds., Advances in environmental measurement methods for asbestos: ASTM Special Technical Publication 1342, p. 53-69.	Structural defects produce planes of weakness called parting
Interdisciplinary	2001	Beard, M.E., Crankshaw, O.S., Ennis, J.T., and Moore, C.E., 2001, Analysis of crayons for asbestos and other fibrous materials, and recommendations for improved analytical definitions: Research Triangle Park, North Carolina, Research Triangle Institute, Center for Environmental Measurements and Quality Assurance, Earth and Mineral Sciences Department, [informal report], 23 p., plus appendices A-H.	NA
Interdisciplinary	2001	Nolan, R.P., Langer, A.M., Ross, M., Wicks, F.J., and Martin, R.F., eds., 2001, The health effects of chrysotile asbestos-contribution of science to risk-management decisions: The Canadian Mineralogist Special Publication 5, 304 p.	NA
Medical	1977	Zielhuis, R.L., 1977, Public health risks of exposure to asbestos: Elmsford, N.Y., Pergamon Press Inc., 143 p.	NA
Medical	1979	Langer, A.M., Rohl, A.N., Wolff, M., and Selikoff, I.J., 1979, Asbestos, fibrous minerals and acicular cleavage fragments-Nomenclature and biological properties, *in* Lemen, R. and Dement, J.M., eds., Dust and disease: Park Forest South, Ill., Pathotox Publishers, p. 1-22.	NA

Table 9. Parting

Community	Year	Source	Parting
Medical	1998	Blake, T., Castranova, V., Schwegler-Berry, D., Baron, P., Deye, G.J., Li, C., and Jones, W., 1998, Effect of fiber length on glass microfiber cytotoxicity: Journal of Toxicology and Environmental Health, v. 54, p. 243-259.	NA
Medical	2001	Ninth Report on Carcinogens, January 2001 http://ehp.niehs.nih.gov/roc/ninth/known/asbestos.pdf	NA
Mineralogical	1914	Dana, E.S., 1914, The system of mineralogy of James Dwight Dana, descriptive mineralogy (6th ed): New York, N.Y., Wiley, p.	...is applied to a separation which is not produced along a plane of minimum cohesion in the lattice but is produced by lamellar twinning, by directed pressure exerted on the crystal, or by oriented inclusions which develop planes of weakness. Parting, in some instances, does not conform to the symmetry requirements of the crystal.
Mineralogical	1977	Campbell, W.J., Blake, R.L, Brown, L.L., Cather, E.E., and Sjober, J.J., 1977, Selected silicate minerals and their asbestiform varieties: U.S. Bureau of Mines Information Circular 8751, 56 p.	The tendency of a crystal or grain to break along crystallographic planes weakened by inclusions or structural defects. Different specimens of the same mineral may or may not exhibit parting. Twinned crystals often part along composition planes, which are lattice planes and therefore, potential crystal faces. Parting is similar to cleavage.
Mineralogical	1979	Campbell, W.J., Steel, E.B., Virta, R.L., and Eisner, M.H., 1979, Relationship of mineral habit to size characteristics for tremolite cleavage fragments and fibers: U.S. Bureau of Mines Report of Investigations 8367, 18 p.	NA
Mineralogical	1980	Bates, R.L., and Jackson, J.A., eds., 1980, Glossary of geology (2d ed.): Falls Church, Va., American Geological Institute, 749 p.	[crystal] The breaking of a mineral along planes of weakness caused by deformation or twinning; e.g. garnet. Cf: cleavage [mineral].
Mineralogical	1982	MacKenzie, W.S., Donaldson, C.H., and Guilford, C., 1982, Atlas of igneous rocks and their textures: New York, N.Y., Wiley, p. 20.	NA
Mineralogical	1987	Dorling, M. and Zussman, J., 1987, Characteristics of asbestiform and non-asbestiform calcic amphiboles: Lithos, v. 20, p. 469-489.	NA

Table 9. Parting

Community	Year	Source	Parting
Mineralogical	1988	Skinner, H.C., Ross, M., and Frondel, C., 1988, Asbestos and other fibrous materials: New York, N.Y., Oxford, 204 p.	NA
Mineralogical	1993	Klein, C. and Hurlbut, C.S., Jr. ,1993, Manual of mineralogy (after James D. Dana) (21st ed.): New York, N.Y., Wiley, 681 p.	When minerals break along planes of structural weakness. The weakness may result from pressure or twinning or exsolution; and, because it is parallel to rational crystallographic planes, it resembles cleavage.
Mineralogical	1993	Veblen, D.R. and Wylie, A.G., 1993, Mineralogy of amphiboles and 1:1 layer silicates in Guthrie Jr., G.D. and Mossman, B.T., eds., Health effects of mineral dusts: Reviews in Mineralogy, v. 28, p. 61-137,	Parting refers to approximately planar breakage along planes that are not cleavage planes.
Mineralogical	2001	Virta, R.L., 2001, Some facts about asbestos: U.S. Geological Survey Fact Sheet FS-012-01, 4 p.	NA
Mineralogical	2002	http://webmineral.com/help/Fracture.html	NA
Mineralogical	2002	http://webmineral.com/help/Habits.html	NA
Regulatory	1974	U.S. District Court, district of Minnesota, 5th Division. Supplemental Memorandum. No. 5-72, Civil 19, Appendix 5, May 11, 1974, p. 24	NA
Regulatory	1976	National Institute for Occupational Safety and Health, 1976, Revised recommended asbestos standard: DHEW (NIOSH) Publication No. 77-169, 96 p.	NA
Regulatory	1983	29 CFR 1910.1001	NA
Regulatory	1990	Ohio Administrative Code (OAC) 3745-20-01	NA
Regulatory	1992	Crane, D., 1992, Polarized light microscopy of asbestos: Occupational Safety and Health Administration Method # ID-191.	NA
Regulatory	1992	Occupational Safety and Health Administration, 1992, Preambles IV. Mineralogical Considerations, National Stone Association and American Mining Congress	NA

Table 9. Parting

Community	Year	Source	Parting
Regulatory	1993	Perkins, R.L. and Harvey, B.W., 1993, Method for the determination of asbestos in bulk building materials: U.S. Environmental Protection Agency EPA/600/R-93/116, Office of Research and Development, Washington, D.C.	NA
Regulatory	1993	Occupational Safety and Health Administration, 1993, Better protection against asbestos in the workplace: U.S. Department of Labor Fact Sheet No. OSHA 93-06. Available on the world wide web at http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=FACT_SHEETS&p_id=144	NA
Regulatory	1995	American Society for Testing and Materials, 1995, Standard test method for microvacuum sampling and indirect analysis of dust by transmission electron microscopy for asbestos structure number concentrations: West Conshohocken, Pa., ASTM 5755-95, 13 p.	NA
Regulatory	1995	International Organization for Standardization, 1995, ISO 10312 Ambient air-determination of asbestos fibres-direct-transfer transmission electron microscopy method (1st ed): Geneve, Switzerland, International Organization for Standardization, 51 p.	NA
Regulatory	1996	Colorado Air Quality Control Commission, 1996, Part B-emission standards for asbestos, *excerpted from* Regulation No. 8 "The control of hazardous air pollutants": Colorado Department of Public Health and Environment, 114 p.	NA
Regulatory	1997	Crane, D., 1997, Asbestos in air: Occupational Safety and Health Administration Method # ID-160.	NA

Table 9. Parting

Community	Year	Source	Parting
Regulatory	1997	NYCRR (New York Code of Rules & Regulations) Title 10 Section 73.1	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools (7-1-01 Edition)	NA
Regulatory	2001	Environmental Protection Agency Part 763-Asbestos Subpart E--Asbestos-Containing Materials in Schools Appendix A (7-1-01 Edition)	NA
Regulatory	2001	29 CFR 1910.1001	NA
Regulatory	2001	30 CFR 56.5001	NA
Regulatory	2001	17 CCR (California Code of Regulations) 93105	NA
Regulatory	2001	West Virginia Code 16-32-2	NA
Regulatory	2002	OAR (Oregon Administrative Rules) 340-248-0010	NA
Regulatory	2002	105 ILCS (Illinois Compiled Statutes Schools) 105/3	NA

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The Composition and Morphology of Amphiboles from the Rainy Creek Complex, Near Libby, Montana

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ABSTRACT

Thirty samples of amphibole-rich rock from the largest mined vermiculite deposit in the world in the Rainy Creek alkaline-ultramafic complex near Libby, Montana, were collected and analyzed. The amphibole-rich rock is the suspected cause of an abnormally high number of asbestos-related diseases reported in the residents of Libby, and in former mine and mill workers. The amphibole-rich samples were analyzed to determine composition and morphology of both fibrous and non-fibrous amphiboles. Sampling was carried out across the accessible portions of the deposit to obtain as complete a representation of the distribution of amphibole types as possible. The range of amphibole compositions, determined from electron probe microanalysis and X-ray diffraction analysis, indicates the presence of winchite, richterite, tremolite, and magnesioriebeckite. The amphiboles from Vermiculite Mountain show nearly complete solid solution between these end-member compositions. Magnesio-arfvedsonite and edenite may also be present in low abundance. An evaluation of the textural characteristics of the amphiboles shows the material to include a complete range of morphologies from prismatic crystals to asbestiform fibers. The morphology of the majority of the material is intermediate between these two varieties. All of the amphiboles, with the possible exception of magnesioriebeckite, can occur in fibrous or asbestiform habit. The Vermiculite Mountain amphiboles, even when originally present as massive material, can produce abundant, extremely fine fibers by gentle abrasion or crushing.

INTRODUCTION

The Rainy Creek alkaline-ultramafic complex (Fig. 1) contains a world-class vermiculite deposit formed by hydrothermal alteration of a large pyroxenite intrusion. The deposit is located at Vermiculite Mountain (also called Zonolite Mountain) approximately six miles northeast of Libby, Montana. The mine began operations circa 1920 and closed in 1990. Recent attention has been given to fibrous and asbestiform amphiboles associated with vermiculite ore produced at Vermiculite Mountain. The amphiboles are suspected to be a causative factor in an abnormally high number of cases of respiratory diseases in the residents of Libby and the former mine and mill workers (Lybarger et al. 2001).

The presence of fibrous and asbestiform amphiboles in the vermiculite and mine waste from Vermiculite Mountain has triggered a Superfund action that ranks among the largest and most costly in the history of the U.S. Environmental Protection Agency. The ultimate resolution of the problems associated with contamination by these materials will be years in coming, and the final costs in both human health and dollars may be enormous. These issues necessitate a very thorough understanding of the morphological and chemical properties of the amphiboles associated with the Vermiculite Mountain deposit. It is these properties that are of ongoing concern with respect to future regulatory policies and investigations into possible mechanisms of toxicity of fibrous and asbestiform amphiboles (Ross 1981; Langer et al. 1991; Kamp et al. 1992; van Oss et al. 1999).

Previous studies of the composition and morphology of the amphiboles from Vermiculite Mountain are limited in number. Wylie and Verkouteren (2000) studied two amphibole samples from the vermiculite mine. They determined the amphibole in both samples to be winchite based in part on chemistry, using the classification system of Leake et al. (1997), and on optical properties. Gunter et al. (2003) confirmed the findings of Wylie and Verkouteren (2000) on the same two samples and analyzed three additional ones, which they also determined to be winchite based on optical microscopy, electron probe microanalysis, and Mössbauer spectroscopy. Indeed, the results of the present study demonstrate convincingly that the vast majority of the amphiboles from Vermiculite Mountain are winchite as currently defined by the International Mineralogical Association (Leake et al. 1997). Previously, the amphibole from Vermiculite Mountain had been called soda tremolite (Larsen 1942), richterite (Deer et al. 1963), soda-rich tremolite (Boettcher 1966b), and tremolite asbestos and richterite asbestos (Langer et al. 1991; Nolan et al. 1991).
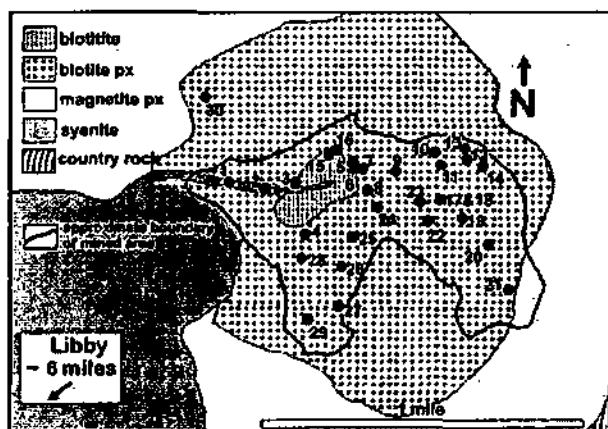
* E-mail: gmeeker@usgs.gov

FIGURE 1. Map of vermiculite mine showing amphibole sampling locations. Geology after Boettcher (1967). The geology, as depicted here, may not completely coincide with the present-day surface geology because of the mining activity between 1967 and 1992. Therefore, the sampling points may not coincide in all cases with the rock units as shown above.

The chemical and physical properties of the fibrous amphiboles from Vermiculite Mountain are of significance for two reasons. The first is that most asbestos regulations specifically cite five amphibole asbestos "minerals:" tremolite, actinolite, anthophyllite, amosite, and crocidolite; and one serpentine mineral, chrysotile. These names have evolved from a combination of mineralogical and industrial terminology. The mineral names richterite and winchite do not appear in existing regulatory language. It is therefore important to understand fully the range of amphibole compositions present so that appropriate terminology can be applied to this material. The second, and perhaps more important reason, is that the mechanisms for the initiation of asbestos-related diseases are not fully understood. If the fibrous and asbestiform amphiboles from Vermiculite Mountain are truly a different type of amphibole than has been studied previously by the medical community, then it is important to understand and describe the full range of chemical and physical properties of this material for future toxicological and epidemiological studies.

The current study was designed to provide a systematic evaluation of the Vermiculite Mountain amphiboles and to specifically answer four important questions: (1) are the amphiboles from Vermiculite Mountain relatively uniform in composition or is there a broad range of compositions; (2) what morphologic characteristics are present within the population of Vermiculite Mountain amphiboles; (3) are there any correlations among chemistry, mineralogy, and morphology; and (4) what are the chemical and physical characteristics of the fibrous and asbestiform amphiboles that are of respirable size? The answers to these questions are of importance to the members of the asbestos community who are involved with developing regulatory language, studying the health effects of asbestos, and planning responsible mining and processing activities. The present study provides a framework with which to evaluate the range of compositions and morphologies of the Vermiculite Mountain am-

phiboles in the context of existing industrial, medical, regulatory, and mineralogical definitions.

GEOLOGIC BACKGROUND

The Rainy Creek complex (Fig. 1) has been described as the upper portion of a hydrothermally altered alkalic igneous complex composed primarily of magnetite pyroxenite, biotite pyroxenite, and biotitite (Pardee and Larsen 1928; Bassett 1959; Boettcher 1966a, 1966b, 1967). The original ultramafic body is an intrusion into the Precambrian Belt Series of northwestern Montana (Boettcher 1966b). A syenite body lies southwest of and adjacent to the altered pyroxenite and is associated with numerous syenite dikes that cut the pyroxenites. A small fenite body has been identified to the north, suggesting the presence of a carbonatite at depth (Boettcher 1967). The amount of vermiculite within the deposit varies considerably. At different locations, the vermiculite content of the ore ranges from 30 to 84% (Pardee and Larsen 1928). Subsequent alkaline pegmatite, alkaline granite, and quartz-rich veins cut the pyroxenites, syenite, and adjacent country rock. It is in the veins and wall rock adjacent to these dikes and veins that a significant portion of the fibrous amphiboles occur as a result of hydrothermal processes (Boettcher 1966b). The dikes, veins, and associated wall-rock alteration zones range in width from a few millimeters to meters, and are found throughout the deposit. Fibrous and massive amphiboles are the most abundant alteration and vein-filling products. Estimates of the amphibole content in the alteration zones of the deposit range from 50 to 75% (Pardee and Larsen 1928). Accessory alteration minerals include calcite, K-feldspar, talc, vermiculite, titanite, pyrite, limonite (formed by pyrite oxidation), albite, and quartz. In addition, "primary" pyroxene, biotite, and hydrobiotite are present in varying amounts.

METHODS

Sample collection

Sampling of the amphibole from Vermiculite Mountain was done in the spring of 2000 with the purpose of collecting a representative suite of amphibole compositions contained within the mined area of the vermiculite deposit. Samples were collected based on a grid designed to provide statistically significant sampling over the accessible areas of the mine. Due to the nature of both the geology of the deposit and the physical conditions in the mine resulting from past reclamation efforts, samples could only be collected from nearly vertical "cut faces" in the mine. We therefore sampled from the closest vertical cut face to each grid node.

A total of 30 locations from the mine area were sampled (Fig. 1). On average, samples were approximately 1–2 kilograms in weight. Samples were selected to provide the maximum variability from location to location in an attempt to fully characterize the range of amphibole compositions and textures present in the deposit. Samples from some locations displayed a massive texture, whereas more friable materials occurred in other locations. In some locations, veins were only a few centimeters in width. At other sampling points, the veins of amphibole-rich rock were as wide as four meters. In these cases, an attempt was made to sample from the edge of the exposed vein as well as the center to look at compositional changes across the vein. In a few cases, veins and adjacent rock appeared to be nearly pure amphibole.

Sample preparation

All of the samples, whether fibrous and friable or massive, produced extremely fine fibrous dust when broken or abraded. The presence of this dust necessitated that all sample preparation steps, including preparation of polished

thin sections, be carried out in a negative-pressure, stainless steel, HEPA-filtered hood. Each sample was examined, as collected, in the hood, and representative pieces were selected for X-ray diffraction (XRD), electron probe microanalysis (EPMA) using wavelength dispersive spectroscopy (WDS), and scanning electron microscopy combined with energy dispersive X-ray analysis (SEM/EDS). For each sample location, an effort was made to find pieces that appeared to be representative of the total sample. Samples selected for EPMA were prepared as polished petrographic thin sections, and detailed optical micrographs were made for later reference. In addition, one or more SEM stubs were prepared for each sample by touching a sample stub covered with a disk of conductive C tape to the inside of each plastic sample bag. This method allowed us to collect and analyze the friable and fibrous components of each sample so that these portions could be distinguished from the non-friable material. The distribution of amphibole types within the friable material could thus be determined. A portion of a typical SEM mount is shown in Figure 2.

Sample analysis

In the present study, we used a combination of three analytical techniques to characterize composition, mineralogy, and morphology of both the fibrous and non-fibrous components of the Vermiculite Mountain amphiboles. None of these analytical techniques alone is capable of accomplishing this task. XRD was used to determine and confirm the presence of amphibole by structural analysis. EPMA/WDS of polished thin-sections was used to derive accurate compositions of the amphiboles present, and SEM/EDS was used to characterize the morphology and to determine the amphibole mineral distribution among individual small fibers that are of respirable size and are generally too small to mount and polish. The SEM-based EDS analysis of small, unpolished fibers does not have the accuracy to definitively identify the amphibole types present. However, when combined and correlated with EPMA/WDS analysis for each individual sample the SEM/EDS analyses show the distributions of the fibrous and asbestiform minerals present in the deposit.

X-ray diffraction analysis

Splits of each sample were analyzed by XRD at the USGS analytical laboratories in Denver. Two grams of material were prepared by hand grinding the sample in an agate mortar and pestle and then wet micronizing (to decrease lattice shear) in a micronizing mill to obtain an average grain size of 5 micrometers. This procedure was used to minimize the orientation effects of the minerals present. The samples were air dried and packed into an aluminum holder for subsequent mineralogical analysis. The powder XRD data were collected using a Philips APD 3720 automated X-ray diffractometer with spinning sample chamber, a diffracted beam monochromator, and Ni-filtered CuKα radiation at 40 kV and 25 mA. The data were collected at room temperature in scanning mode, with a step of 0.02 °2θ and counting time of 1 second at each step. The collected data were evaluated and minerals were identified using JADE+ software from Materials Data Inc.[1]

Qualitative mineralogy was determined for each sample as major (>25% by weight), minor (5–25%), and trace (<5%). Our detection limit for these analyses was approximately 1–2 wt%. Table 1 shows samples ranging from fairly pure amphibole (samples 25, 28, and 30) to complex mixtures of many minerals (samples 7, 11, and 16). The primary amphibole minerals identified in each sample by matching reference X-ray data (JADE+) were winchite and richterite. Other minerals identified as major in some samples included calcite, talc, and dolomite. Minerals present at the minor level in many of the samples include calcite, K-feldspar, pyroxene, hydrobiotite, talc, quartz, vermiculite, and biotite.

The arrangement of the amphiboles into subgroups and series based on crystal-chemical considerations (Leake et al. 1997) is to a large extent a matter of convenience; considerable solid solution exists between one series and another, and even between one subgroup and another. Therefore, it is imperative that the final assignment of a specific amphibole name be based on a high-quality chemical analysis of the sample.
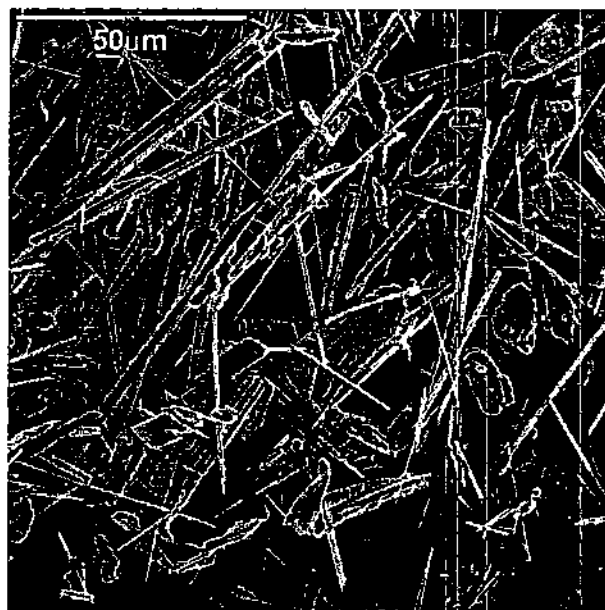

FIGURE 2. Area of the surface of a typical SEM sample stub prepared by touching the stub to the inside of the plastic sample bag. Most of the particles in the image are amphibole. Particle morphologies include acicular structures with high to low aspect ratios, bundles, and prismatic crystals. A few curved fibers can be seen in the image. Scale bar is 50 μm.

TABLE 1. Qualitative mineralogy by XRD

SAMPLE	MAJOR	MINOR	TRACE
1	rht/wht, tlc		qtz, kfs, vrm
2	rht/wht	cal	qtz, kfs,dol
3	rht/wht,cal	kfs	bt
4	rht/wht	tlc, aug, hbt	cal, dol
5	rht/wht	cal, kfs	hbt
6	rht/wht, cal		qtz, kfs
7	rht/wht	cal, aug	bt, vrm, kfs
8	rht/wht	cal	tlc, vrm, kfs, bt
9	rht/wht	cal	vrm, dol
10	rht/wht	cal, vrm	
11	rht/wht	cal, aug, kfs, tlc	qtz, vrm
12	rht/wht	kfs	
13	rht/wht	cal, tlc, di, kfs	
14	rht/wht	bt, kfs	cal, dol
15	rht/wht	cal, tlc	kfs
16	rht/wht	cal, aug, tlc, vrm	qtz, kfs
17	rht/wht	kfs, cal	bt
18	rht/wht	cal, kfs	bt
19	rht/wht	cal, kfs, aug	bt
20	rht/wht	cal	vrm
21	rht/wht	cal, tlc, hbt	kfs
22	rht/wht	cal, hbt, kfs	tlc
23	rht/wht	cal, kfs	
24	rht/wht	cal, kfs	
25	rht/wht		kfs, cal
26	rht/wht	cal, kfs, vrm	tlc, dol
27	rht/wht, cal		kfs
28	rht/wht		vrm, hbt
29	rht/wht, cal, dol		kfs
30	rht/wht	kfs	

Notes: Estimated concentration reported as major (>25 wt%), minor (>5%, <25%), and trace (<5%). Amphibole identification was determined by pattern structure using a best fit algorithm. Positive identification of amphiboles must rely on chemistry (see text). Mineral abbreviations used: rht/wht = richterite/winchite, tlc = talc, qtz = quartz, cal = calcite, kfs = potassium feldspar, vrm = vermiculite, dol = dolomite, bt = biotite, aug = augite, hbt = hydrobiolite, di = diopside.

Scanning electron microscopy and energy dispersive X-ray analysis

Images were obtained of representative areas of each sample stub (Fig. 2). Thirty or more fibers were analyzed in each of the 30 samples. Isolated fibers with diameters of 3 μm and less, representing the respirable fraction, were selected for analysis so as to minimize contributions of stray X-ray counts from nearby phases both laterally and vertically. One or more of the analyses from each sample set were discarded after later determination that the analysis contained unacceptable cation ratios, possibly due to contributions from adhering or nearby particles.

Scanning electron microscopy was performed using a JEOL 5800LV instrument, at the US Geographical Survey in Denver, operating in high-vacuum mode. Energy dispersive X-ray analysis was performed using an Oxford ISIS EDS system equipped with an ultra-thin-window detector. Analytical conditions were: 15 kV accelerating voltage, 0.5–3 nA beam current (cup), and approximately 30% detector dead time. All SEM samples were C coated. Data reduction was performed using the Oxford ISIS standardless analysis package using the ZAF option. Analyses were normalized to 100%. The quality of each EDS analysis was based on cation ratios and correlation with EPMA/WDS data (see below).

The matrix corrections used in these EDS analyses do not account for particle geometry. It is well known that such errors can be significant. However, Small and Armstrong (2000) have shown that, at 10–15 kV accelerating voltage, geometry-induced errors on particles can be relatively small. Our errors, in relative weight percent, estimated from analysis of 0.5–10 μm diameter particles of USGS, BIR1-G basalt glass reference material (Meeker et al. 1998) are approximately ±13% (1σ) for Na_2O, 4% for MgO and CaO, 3% for Al_2O_3, 2% for SiO_2, and 7% for FeO.

In addition to chemical EDS data on amphiboles from each sample stub, samples 4, 10, 16, 20, and 30 were selected for morphologic analysis of the amphibole particles. These samples were chosen to provide a representative range of compositions and textures. Size measurements were made using the Oxford ISIS software calibrated with a certified reference grid. For each sample, every amphibole (identified by EDS) was measured within a randomly chosen, 100 × 100 μm area of the stub. The minimum total number of particles counted was 300 per sample. One sample contained fewer than 300 amphiboles in one field of view, so a second field, not overlapping the first, approximately 25 × 25 μm in size was used to complete the data collection, using the same method as above. The maximum length and average width of each amphibole contained within or crossing into the field of view was used to calculate the aspect ratio (length/width) of each amphibole particle.

Wavelength-dispersive electron probe microanalysis

Electron microprobe analysis was performed on polished thin sections of 14 samples. The samples were selected based on their textural characteristics, mineralogy as determined by XRD and SEM/EDS, optical properties, and how representative the samples appeared to be of the entire suite. An attempt was made to include the full range of chemistries and textures.

Quantitative EPMA of the samples was performed using a five-wavelength spectrometer (WDS), fully automated, JEOL 8900 scanning electron microprobe, at the USGS in Denver. Analyses were obtained from areas that appeared to be representative of each sample by optical microscopy. Analytical conditions were: 15 kV accelerating voltage, 20 nA beam current (cup), point beam mode, and 20 second peak and 10 second background counting time. Calibration was performed using well-characterized silicate and oxide standards. Analytical precision for major and minor elements based on replicate analysis of standards was better than ±2% relative concentration for major and minor elements and equal to counting statistics for trace (<1 wt%) elements. Matrix corrections were performed with the JEOL 8900 ZAF software.

The friable nature of most of the samples caused some areas of the thin sections to exhibit plucking or poor polishing. Analyses within these areas commonly resulted in lower totals than would normally be acceptable on a polished surface. We rejected any EPMA analysis with an oxide total lower than 92 wt% (calculated H_2O in the Vermiculite Mountain amphiboles ranges from 1.72–2.11 wt%). The quality of the remaining analyses were judged by cation ratios. Analyses with unacceptable cation ratios (see below) were not included in the data reduction.

DATA ANALYSIS

The amphibole classification system of Leake et al. (1997) is based on site assignments for each cation in the structure. An accurate amphibole classifica-

tion based on chemical analysis requires determination of the OH, ultra-light elements (Z < 8), and halogen content, as well as the oxidation state of Fe. Our EPMA analyses of the thin sections included F and Cl. It is not possible to analyze for OH, nor is it possible to accurately determine the ultra-light element content, particularly Li, by EPMA. It is unlikely, however, that Li is present in significant amounts because wet-chemical analyses of Vermiculite Mountain amphibole by previous investigators did not indicate Li (Deer et al. 1963). Also, USGS trace-element analyses of the 30 samples by ICRMS revealed Li (and other possible elemental constituents) at levels too low to be significant in cation calculations (P. J. Lamothe, personal communication). Finally, the stoichiometry that was evident upon data reduction of the EPMA data indicates that no significant components are missing from the analyses. The hydroxyl ion $(OH)^-$ was accounted for by the method described in Leake et al. (1997) by assuming a total anion charge of –2 for F + Cl + (OH).

Analyses were judged primarily on cation ratios for data corrected to 23 O atoms. Cations were assigned to crystallographic sites based on the methods outlined in Leake et al. (1997). In particular, all Si was assigned to the tetrahedral or T-site, followed by Al and then Ti, until the tetrahedral cation total equaled 8.00. Remaining Al and Ti, followed by Fe^{3+}, Mg, Fe^{2+}, and Mn, in that order, were assigned to the octahedral C-sites (M1, M2, and M3) until the C-site total equaled 5, or slightly less in some cases. Any remaining C-site cations, followed by Ca and Na, were assigned to the B-site (M4) until the site total equaled 2. All K and any remaining Na were assigned to the A-site. Because the Vermiculite Mountain amphiboles only include sodic, sodic-calcic, and calcic amphiboles as defined by Leake et al. (1997), it is primarily the distribution and cation totals of Ca, Na, and K in the B- and A-sites, and Mg/(Mg + Fe^{2+}) that determine the amphibole species.

A complete and correct application of the Leake et al. (1997) classification method requires knowledge of the oxidation state of Fe. Gunter et al. (2003), have determined Fe^{3+}/Fe^{total} in five samples of Vermiculite Mountain amphiboles to range from 0.56 to 0.76 using Mössbauer spectroscopy. Because of the large range of compositions of the amphiboles, we compared the results of calculating total Fe as Fe^{2+} vs. total Fe as Fe^{3+}. The difference in the handling of Fe made a small but significant difference in the distribution of the calculated amphibole species. Many analyses showed a change in mineral classification, as seen in Figure 3. The calculated stoichiometry of all EPMA analyses improved when total Fe was calculated as Fe^{3+}. In particular, the average number of Si cations based on 23 O atoms (anion charge = 46.0) decreased from 8.08 ± 0.07 with total Fe calculated as Fe^{2+} to 7.96 ± 0.06 with total Fe calculated as Fe^{3+}. Because the maximum Si content of the T-site in amphibole must be less than or equal to 8, within analytical error, these results suggest $Fe^{3+} > Fe^{2+}$, in agree-
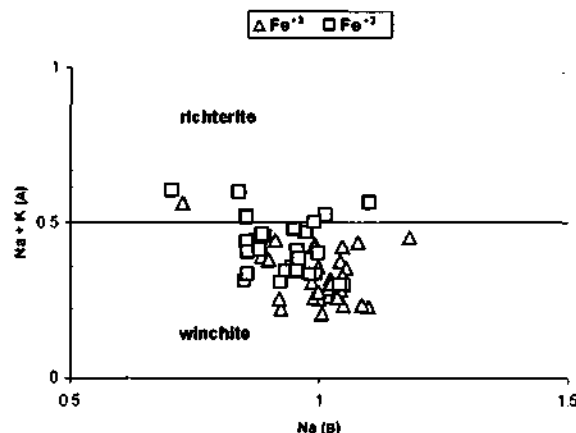

FIGURE 3. EPMA data from sample 14 plotted with all Fe calculated as Fe^{2+} and the same analyses plotted with all Fe calculated as Fe^{3+}. The Y-axis represents the amount of Na + K in the A-site of the amphibole structure, and the X-axis the amount of Na in the B-site. The boundary between winchite and richterite, as defined by Leake et al. (1997), is shown as a horizontal line at $^A(Na+K) = 0.5$. Note the approximate 25% decrease in the number of points plotting in the richterite field when all Fe is calculated as Fe^{+3}.

ment with the results of Gunter et al. (2003). To arrive at a better estimation of Fe^{3+}/Fe^{total} for each amphibole mineral, we chose 169 of the best EPMA analyses, representing a full range of compositions, and calculated Fe^{3+}/Fe^{total} for each individual analysis. The value for Fe^{3+}/Fe^{total} was determined by minimizing the deviation from ideal stoichiometry as described in Leake et al. (1997).

The average Fe^{3+}/Fe^{total} calculated from the best 169 EPMA analyses was 0.60, compatible with the values determined by Gunter et al. (2003). This average value was used to calculate the mineral distributions for the EDS analyses. This number will be least accurate for compositions close to tremolite and magnesioriebeckite (see below). However, the error introduced by using $Fe^{3+}/Fe^{total} = 0.60$ for all EDS analyses is significantly less than the analytical error for most of the major elements determined by EDS.

Amphibole classification derived from EDS results was also based on Leake et al. (1997). In general, the EDS data were very similar to the quantitative WDS results from EPMA. It was found, however, that the C-site totals from the EDS data averaged 3% below the ideal 5 cations. This deficiency could be due to the less-accurate standardless quantification routine, the fact that the analyses were performed on individual thin fibers rather than a polished surface or, more likely, a combination of both. In the Vermiculite Mountain amphibole, the primary cations in the C-site are Mg and Fe. In the cation site calculations, upon filling the C-site, any remaining C-site cations would be placed into the B-site. Increased residual C-site cations in the B-site would decrease the amount of Na in the B-site and increase the amount of Na in the A-site, thereby affecting the cation distributions and possibly the amphibole species classification. However, in our calculations using the more accurate EPMA/WDS data, residual C-site cations in the B-site were generally low or not present. Therefore, low totals in the C-site in the EDS data for these amphiboles should not cause significant errors in amphibole classification.

We attribute our low C-site totals in the EDS data to particle geometry and associated matrix correction errors primarily affecting Fe and possibly Mg, and not to actual differences between the friable and non-friable minerals in the Vermiculite Mountain amphibole. Based on our estimated analytical error for Fe and Mg, derived from the analysis of basalt glass particles (see above), and on the overall quality of each EDS analysis, we chose to incorporate EDS data points in which the C-site totals were 4.7 or higher or within 94% of the ideal 5 cations. With this error, the calculated compositions and site assignments on individual EDS analyses did not appear to change significantly or affect the mineral classification relative to the WDS data. A check on the validity of this argument can be seen in the sample-by-sample correlation of compositional distributions showing good agreement between EPMA/WDS and SEM/EDS data (Fig. 4). It is interesting to note that if the error in the C-site totals in the EDS data had been high rather than low, the distribution of amphibole species in the friable materials would likely have been skewed. An error of this type would be difficult to detect without EPMA/WDS data for comparison.

RESULTS

Chemistry

In general, the WDS (from EPMA) and the EDS data agree with respect to the amphibole species represented in each sample (Fig. 4). For some samples, the EPMA data show a narrower compositional range than the EDS data. This result is reasonable because EPMA analyses were performed on a single polished thin section for each sample, which may not represent the entire range of compositions of friable material found in a sample.

The data indicate that most of the Vermiculite Mountain amphiboles can be classified as one of three types, although it is possible that as many as six different amphiboles may be present, based on the Leake et al. (1997) classification criteria. Those minerals, in order of decreasing abundance, are: winchite, richterite, tremolite, and possibly magnesioriebeckite, edenite (see below), and magnesio-arfvedsonite. Representative EPMA analyses of the amphibole minerals are given in Table 2. For the respirable fraction, as determined by SEM/EDS, approximately 84% of the amphiboles can be classified as winchite,
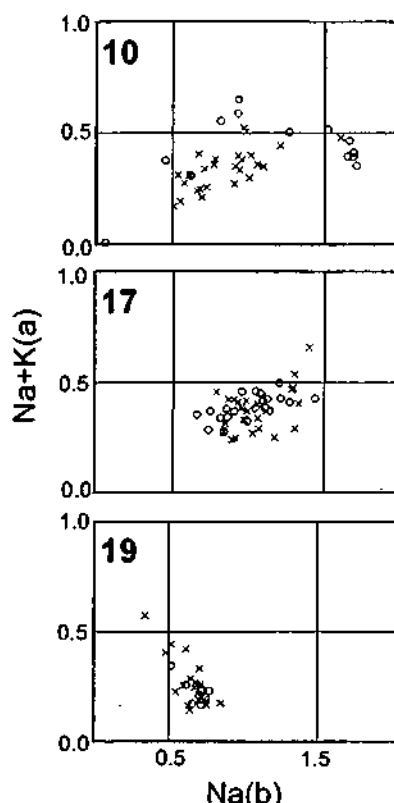

FIGURE 4. Cation values for Na in the B-site and Na + K in the A-site from individual samples show typical correlation between SEM (crosses) and EPMA (circles) data. Sample numbers are in the upper left corner of each plot.
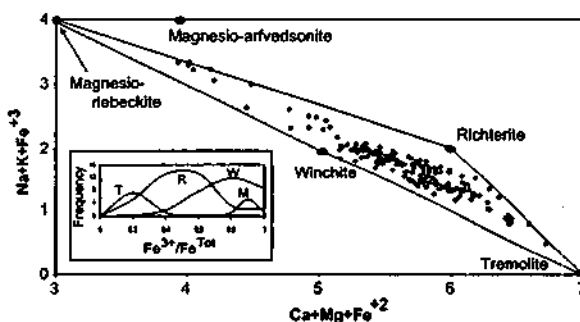

FIGURE 5. Amphibole compositions from the best 169 EPMA analyses, as determined from cation ratios, based on the criteria of Leake et al. (1997). End-member points for tremolite, winchite, richterite, magnesioriebeckite, and magnesio-arfvedsonite are shown. The data suggest that complete solid-solution may exist within the region defined by the tremolite, winchite, richterite, and magnesioriebeckite. Also shown (inset) are "best-fit" curves for the same data, showing calculated Fe^{3+}/Fe^{total} (see text) values for individual minerals where T=tremolite, R=richterite, W=winchite (multiplied by 0.25), and M=magnesioriebeckite.

11% as richterite, and 6% as tremolite.

Figure 5 shows the distribution of amphibole compositions found at the mine site at Vermiculite Mountain. The amphiboles range from nearly pure tremolite to compositions

TABLE 2. Representative wavelength dispersive of amphibole minerals

Sample	12	12	14	16	17	24	24	25	10	16	16
Mineral	W	W	W	W	W	W	W	W	T	T	T
Wt% Oxides											
F	0.21	0.27	0.18	0.20	0.58	0.31	0.52	0.43	0.21	0.17	0.20
Na_2O	3.39	4.45	4.21	3.29	3.54	3.13	4.47	2.70	2.61	2.26	2.27
MgO	22.3	19.2	20.5	21.4	19.8	21.3	20.9	21.7	22.0	23.0	22.0
Al_2O_3	0.15	0.17	0.16	0.46	0.37	0.15	0.33	0.11	0.16	0.60	0.52
SiO_2	58.7	57.1	57.2	57.7	56.8	57.5	57.7	57.5	57.1	56.4	56.6
Cl	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
K_2O	0.65	0.71	1.03	1.02	0.94	0.93	1.10	0.62	0.71	0.87	0.78
CaO	7.50	5.18	6.28	9.41	7.51	8.43	6.62	9.89	10.2	10.1	10.3
TiO_2	0.14	0.14	0.13	0.07	0.17	0.04	0.23	0.07	0.12	0.10	0.09
MnO	0.10	0.05	0.06	0.14	0.14	0.13	0.08	0.10	0.09	0.08	0.08
FeO-T	5.71	8.38	6.35	4.38	6.54	4.95	5.54	4.22	3.08	2.48	2.47
$O \equiv F,Cl$	0.09	0.11	0.07	0.08	0.24	0.13	0.22	0.18	0.09	0.07	0.08
□TOTAL	98.79	95.54	96.00	97.99	96.21	96.73	97.21	97.12	96.19	95.92	95.19
Structural Formula											
Si	7.988	8.000	7.990	7.987	7.993	7.988	7.987	7.994	7.997	7.904	7.986
Al^{iv}	0.012	0.000	0.010	0.013	0.007	0.012	0.013	0.006	0.003	0.096	0.014
Sum T-site	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al^{iv}	0.012	0.029	0.016	0.062	0.054	0.012	0.040	0.011	0.023	0.004	0.073
Ti	0.015	0.015	0.014	0.008	0.018	0.004	0.024	0.007	0.012	0.010	0.010
Fe^{+4}	0.340	0.981	0.682	0.052	0.498	0.415	0.524	0.178	0.038	0.024	0.036
Mg	4.531	3.976	4.264	4.423	4.153	4.421	4.306	4.489	4.599	4.813	4.627
Fe^{2+}	0.103	0.000	0.024	0.455	0.271	0.147	0.106	0.313	0.323	0.149	0.254
Mn	0.000	0.000	0.000	0.001	0.005	0.000	0.000	0.001	0.006	0.000	0.000
Sum C-site	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
Mg	0.000	0.031	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe^{2+}	0.207	0.000	0.035	0.000	0.000	0.013	0.011	0.000	0.000	0.118	0.001
Mn	0.011	0.006	0.007	0.015	0.012	0.015	0.009	0.010	0.005	0.010	0.009
Ca	1.093	0.777	0.939	1.396	1.131	1.256	0.982	1.473	1.536	1.511	1.552
Na	0.688	1.187	1.018	0.589	0.858	0.716	0.998	0.517	0.459	0.362	0.438
Sum B-site	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.207	0.021	0.121	0.293	0.109	0.127	0.203	0.210	0.249	0.253	0.183
K	0.112	0.128	0.183	0.179	0.168	0.165	0.195	0.109	0.128	0.156	0.140
Sum A-site	0.319	0.148	0.303	0.473	0.276	0.293	0.398	0.320	0.377	0.409	0.323
Total Cations	15.319	15.148	15.303	15.473	15.276	15.293	15.398	15.320	15.377	15.409	15.323

Notes: W = winchite, R = richterite, T = tremolite, MR = magnesioriebeckite, MA = magnesio-arfvedsonite, BDL = below detectability limit. Ferric Fe determined by stoichiometry. *continued*

approaching end-member magnesioriebeckite. The majority of the compositions lie within the ternary field temolite-winchite-richterite, and all compositions lie within the field tremolite-richterite-magnesioriebeckite. The distribution of compositions suggests that complete solid solution exists within the compositional field shown. These results are compatible with the study by Melzer et al. (2000), who found evidence for complete solid solution in the experimental system K-richterite-richterite-tremolite.

Figure 5 also shows the distributions of Fe^{3+}/Fe^{total} for each amphibole species. These distributions suggest that Fe^{3+} is partitioned into each amphibole mineral according to crystal-chemical requirements. The complexities of such substitutions and the difficulties in identifying a specific substitution mechanism in amphiboles were discussed by Popp and Bryndzia (1992).

Actinolite was not found in our analyses of the Vermiculite Mountain amphiboles. Wylie and Verkouteren (2000) speculated on the presence of actinolite but were not able to make a determination in their samples because they did not calculate or otherwise determine the Fe^{3+} content. If our EPMA analyses were calculated with all Fe as Fe^{2+}, some of the analyses would be classified as actinolite, based on Leake et al. (1997). This

finding suggests that during routine semi-quantitative analyses of Vermiculite Mountain amphibole, as might be performed by an environmental asbestos analysis laboratory, the presence of actinolite might be reported. It is also possible that different laboratories could report the presence of different asbestos minerals from the same samples depending on the data reduction methods used.

Both SEM/EDS single-fiber and EPMA/WDS thin-section data occupy approximately the same compositional space, as shown in Figure 6. A few compositions that correspond to magnesioriebeckite and one to magnesio-arfvedsonite are indicated from the EPMA data. These amphibole types along with edenite (not identified in the EPMA data) were also found with SEM/EDS analyses. The magnesioriebeckite and magnesio-arfvedsonite EDS data points are all within 1σ error of richterite and/or winchite. The lack of statistically significant EDS data for magnesioriebeckite and magnesio-arfvedsonite suggests that these minerals may not exist in fibrous form. All of the EDS edenite analyses are within 2σ error of being classified as tremolite. All other minerals were identified in both thin sections and in the single fiber data. This comparison indicates that tremolite, winchite, and richterite (and possibly edenite) all occur

TABLE 2. -- continued (2)

Sample	16	20	25	25	25	10	12	14	16	24	30
Mineral	T	T	T	T	T	R	R	R	R	R	R
Wt% Oxides											
F	0.18	0.00	0.08	0.47	0.21	0.65	0.08	0.17	0.34	0.74	0.52
Na_2O	2.26	1.29	2.62	2.49	2.28	4.13	3.73	4.38	4.96	3.90	4.48
MgO	22.1	21.7	21.9	21.9	21.9	23.0	21.1	20.3	19.8	21.2	21.4
Al_2O_3	0.71	0.56	0.30	0.32	0.25	0.01	0.12	0.20	0.29	0.36	0.27
SiO_2	55.6	55.2	57.3	57.3	57.3	58.1	55.3	55.2	56.2	56.8	56.9
Cl	0.02	0.03	0.01	BDL	BDL	0.01	BDL	BDL	BDL	0.01	BDL
K_2O	0.86	0.58	0.78	0.75	0.68	1.56	0.77	1.06	0.97	1.20	1.22
CaO	10.1	10.70	10.2	10.3	10.5	7.79	7.45	6.11	5.76	8.03	7.43
TiO_2	0.11	0.10	0.01	0.04	0.06	0.20	0.21	0.12	0.04	0.07	0.16
MnO	0.07	0.10	0.10	0.10	0.10	0.09	0.05	0.09	0.08	0.13	0.12
FeO	2.40	4.00	3.73	3.82	3.52	2.35	5.61	6.56	7.49	5.08	5.08
O≡F,Cl	0.08	0.01	0.04	0.20	0.09	0.28	0.03	0.07	0.14	0.31	0.22
☐TOTAL	94.32	94.24	96.96	97.21	96.63	97.59	94.33	94.13	95.73	97.25	97.34
Structural Formula											
Si	7.918	7.911	7.977	7.972	7.992	7.999	7.980	7.983	7.976	7.967	7.973
Al[IV]	0.082	0.089	0.023	0.028	0.008	0.001	0.020	0.017	0.024	0.033	0.027
Sum T-site	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al[IV]	0.037	0.006	0.026	0.025	0.034	0.001	0.001	0.017	0.024	0.026	0.016
Ti	0.012	0.011	0.001	0.004	0.006	0.021	0.022	0.013	0.004	0.007	0.017
Fe^{3+}	0.101	0.036	0.070	0.073	0.073	0.226	0.004	0.240	0.485	0.150	0.094
Mg	4.686	4.629	4.547	4.535	4.550	4.727	4.534	4.374	4.179	4.433	4.465
Fe^{2+}	0.163	0.318	0.355	0.363	0.337	0.026	0.438	0.355	0.307	0.383	0.407
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sum C-site	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe^{2+}	0.021	0.126	0.008	0.009	0.001	0.019	0.234	0.198	0.097	0.062	0.094
Mn	0.008	0.012	0.012	0.012	0.012	0.010	0.006	0.010	0.009	0.015	0.014
Ca	1.542	1.643	1.520	1.537	1.562	1.150	1.151	0.946	0.875	1.206	1.115
Na	0.429	0.219	0.460	0.442	0.425	0.821	0.608	0.846	1.018	0.716	0.777
Sum B-site	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.194	0.138	0.247	0.231	0.192	0.281	0.437	0.383	0.348	0.343	0.441
K	0.155	0.106	0.138	0.134	0.121	0.274	0.141	0.196	0.176	0.215	0.218
Sum A-site	0.350	0.244	0.385	0.364	0.313	0.554	0.578	0.579	0.524	0.558	0.659
Total Cations	15.350	15.244	15.385	15.364	15.313	15.554	15.578	15.579	15.524	15.558	15.659

in fibrous or asbestiform habit in the Vermiculite Mountain rocks, and also that the EPMA data include the majority of the suite of amphibole compositions that are present in the deposit.

The EDS single-fiber data provide information on the distribution of compositions of the friable and fibrous amphiboles. These analyses are plotted for each sample in Figure 7. For many samples, the compositions cluster in relatively small regions of the diagram as compared to Figure 6. A few samples, such as 8, 16, and 23, show a wider range of compositions. Compositions of several of the samples (5, 7, 9, 13, 21, and 24) cluster entirely within the winchite region of the diagram. Several samples (1, 3, 6, 25, 28, and 29) have a significant amount of richterite, but no samples plot entirely within the richterite field. Samples 8, 20, and 23 show the highest concentrations of tremolite.

The classification of a small portion of the Vermiculite Mountain amphibole as edenite (samples 4, 8, and 19) by EDS remains uncertain. A natural occurrence of fibrous fluoro-edenite from Sicily was reported by Gianfagna and Oberti (2001). It is likely, however, that in our analyses, microcrystalline calcite, intergrown with the amphibole, could be contributing Ca to the totals, thus increasing the amount of Na assigned to the A-site. Nevertheless, some of our SEM/EDS analyses

calculate as edenite with no evidence of calcite. However, these analyses are within analytical error of tremolite and richterite.

Edenite usually contains Al in the T-site to balance Na in the A-site, which was not found in the Vermiculite Mountain amphibole. The classification scheme of Leake et al. (1997) is not clear with regard to calcic amphiboles of this composition, i.e., amphiboles containing more than 0.5 (Na + K) in the A-site, less than 0.5 Na in the B-site, and more than 7.5 Si in the T-site. Leake (1978) includes the term "silicic-edenite," which would cover the compositions found in the Vermiculite Mountain amphibole. This name was dropped in the subsequent and final classification system (Leake et al. 1997) and it appears that the intended name for amphiboles of this composition is edenite. Further investigations are underway regarding the presence of edenite.

Morphology

In general, the Vermiculite Mountain amphiboles have two types of occurrence: vein-fillings and replacement of the primary pyroxene of the Rainy Creek complex. The textures displayed by the amphibole and associated minerals are indicative of their hydrothermal origin. Traditionally, amphibole asbestos is thought to occur as a vein-filling mineral formed during

hydrothermal alteration in a tensional environment (Zoltai 1981) or as a low-temperature alteration product formed in a stress-free environment (Dorling and Zussman 1987). In a substantial portion of our samples, the amphiboles appear to be forming as direct replacements of pyroxene, probably by the infiltration of fluids in microfractures. Examples of these two modes of formation are shown in Figure 8. Figure 8a shows a cross-section of a vein filled with symmetrically matching layers of amphibole and other minerals including calcite, K-feldspar, titanite, and pyrite. The amphibole becomes finer-grained toward the vein center but the composition of the winchite amphibole remains fairly constant across the vein. Figure 8b shows a portion of a sample in which the primary pyroxene augite crystals are being replaced by fibrous amphibole winchite and richterite. Figure 8c shows a detailed view of this replacement within a single pyroxene crystal. The long axis of the fibrous amphibole is crystallo-graphically aligned with the original pyroxene crystal.

In portions of all of the samples studied, the amphibole is intergrown with accessory minerals such as calcite, K-feldspar, quartz, and titanite. The accessory minerals range in size from millimeters to sub-micrometer. Extremely fine-grained crystals of these minerals are commonly intergrown and often crystallographically oriented with the amphibole (Fig. 9). These minerals were found in thin section as well as in the SEM samples of friable dust, often in acicular form.

The Vermiculite Mountain amphiboles show a range of morphologies from prismatic to asbestiform (Fig. 10). Much of the fibrous amphibole seen in the SEM micrographs (Figs. 2 and 10) is composed of acicular and, some cases, needle-like particles. Splayed ends and curved fibers are present, but are not particularly common. Fibril diameter in the Vermiculite Mountain asbestiform amphibole ranges from approximately 0.1 to 1 μm. Individual fibrils less than 0.2 μm in diameter are rare, and fiber bundles are often composed of different-sized fibrils. Many of the characteristics generally associated with "commercial-grade" asbestos, such as curved fibers and bundles with splayed ends (Perkins and Harvey 1993) are present but are not common in the Vermiculite Mountain amphibole.[2] The material, however, is very friable and even gentle handling of what appears to be a solid, coherent rock can liberate very large numbers of extremely fine fibers as seen in SEM images (Figs. 2 and 10) and in size-distribution plots of material sampled from the inside of the sample bags (Fig. 11).

TABLE 2 --continued (3)

Sample	30	30	10	10	10	10	10	12	10
Mineral	R	R	MR	MR*	MR*	MR*	MR*	MR	MA
Wt% Oxides									
F	0.56	0.17	0.45	0.30	0.27	0.45	0.49	0.09	0.52
Na₂O	4.59	4.26	7.04	7.11	6.92	6.85	6.98	6.51	6.76
MgO	20.9	21.0	17.1	16.8	16.4	16.8	17.0	17.5	17.8
Al₂O₃	0.45	0.35	0.04	0.07	0.08	0.07	0.08	0.25	0.08
SiO₂	57.3	56.6	56.5	57.1	56.8	56.9	56.9	56.4	56.8
Cl	BDL	BDL	0.01	BDL	BDL	BDL	0.01	BDL	BDL
K₂O	1.29	1.32	1.09	0.95	0.96	0.98	0.97	0.81	1.06
CaO	7.31	7.26	2.03	2.07	1.92	2.32	2.07	2.20	2.70
TiO₂	0.05	0.04	0.47	0.15	0.39	0.44	0.41	0.58	0.25
MnO	0.12	0.06	0.07	0.09	0.05	0.09	0.08	0.04	0.04
FeO	5.29	5.22	11.5	12.3	12.3	11.4	11.3	11.0	11.0
O ≡ F,Cl	0.23	0.07	0.19	0.13	0.11	0.19	0.21	0.04	0.22
OTOTAL	97.65	96.16	96.15	96.76	96.06	96.13	96.03	95.39	96.89
Structural Formula									
Si	7.979	7.971	7.997	8.006	8.011	8.022	8.012	7.980	7.993
Alⁱᵛ	0.021	0.029	0.003	0.000	0.000	0.000	0.000	0.020	0.007
Sum T-site	8.000	8.000	8.000	8.006	8.011	8.022	8.012	8.000	8.000
Alᵛⁱ	0.053	0.029	0.004	0.012	0.013	0.011	0.013	0.020	0.007
Ti	0.005	0.004	0.049	0.016	0.042	0.046	0.043	0.062	0.026
Fe³⁺	0.241	0.285	1.097	1.240	1.272	1.177	1.211	1.123	0.955
Mg	4.348	4.402	3.604	3.505	3.456	3.532	3.578	3.690	3.738
Fe²⁺	0.354	0.280	0.246	0.200	0.182	0.164	0.115	0.105	0.274
Mn	0.000	0.000	0.000	0.011	0.006	0.011	0.009	0.000	0.000
Sum C-site	5.000	5.000	5.000	4.984	4.972	4.942	4.968	5.000	5.000
Mg	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe²⁺	0.021	0.050	0.023	0.000	0.000	0.000	0.000	0.074	0.067
Mn	0.014	0.007	0.009	0.000	0.000	0.000	0.000	0.005	0.005
Ca	1.091	1.096	0.307	0.310	0.290	0.350	0.313	0.333	0.407
Na	0.875	0.847	1.662	1.690	1.710	1.650	1.687	1.588	1.521
Sum B-site	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Na	0.364	0.316	0.270	0.243	0.181	0.221	0.220	0.196	0.323
K	0.229	0.238	0.196	0.170	0.173	0.175	0.173	0.146	0.191
Sum A-site	0.593	0.554	0.466	0.414	0.354	0.396	0.393	0.341	0.513
Total Cations	15.593	15.554	15.466	15.403	15.336	15.360	15.373	15.341	15.513

* These analyses display T site totals slightly higher than what is recommended by Leake et al. (1997) for determination of percent Fe³⁺, however, the T site error is well below 1% and Fe³⁺ values are in agreement with other analyses of similar composition.
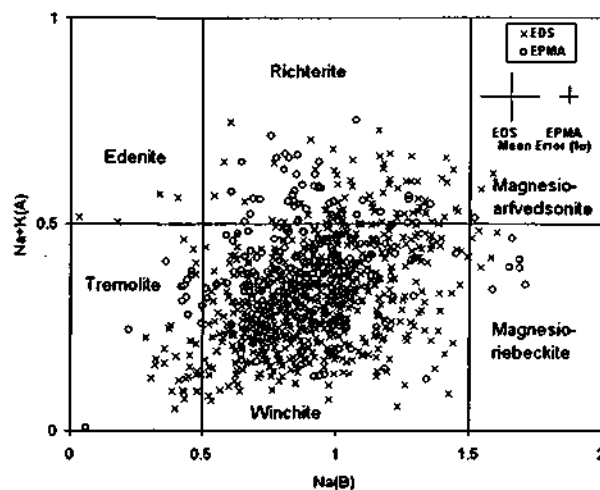
FIGURE 6. EPMA/WDS and SEM/EDS data showing the entire range of amphibole species found from all 30 samples. See text for details.

[2] The definition of asbestiform found in Perkins and Harvey (1993) is for optical identification of commercial-grade asbestos used in building materials.
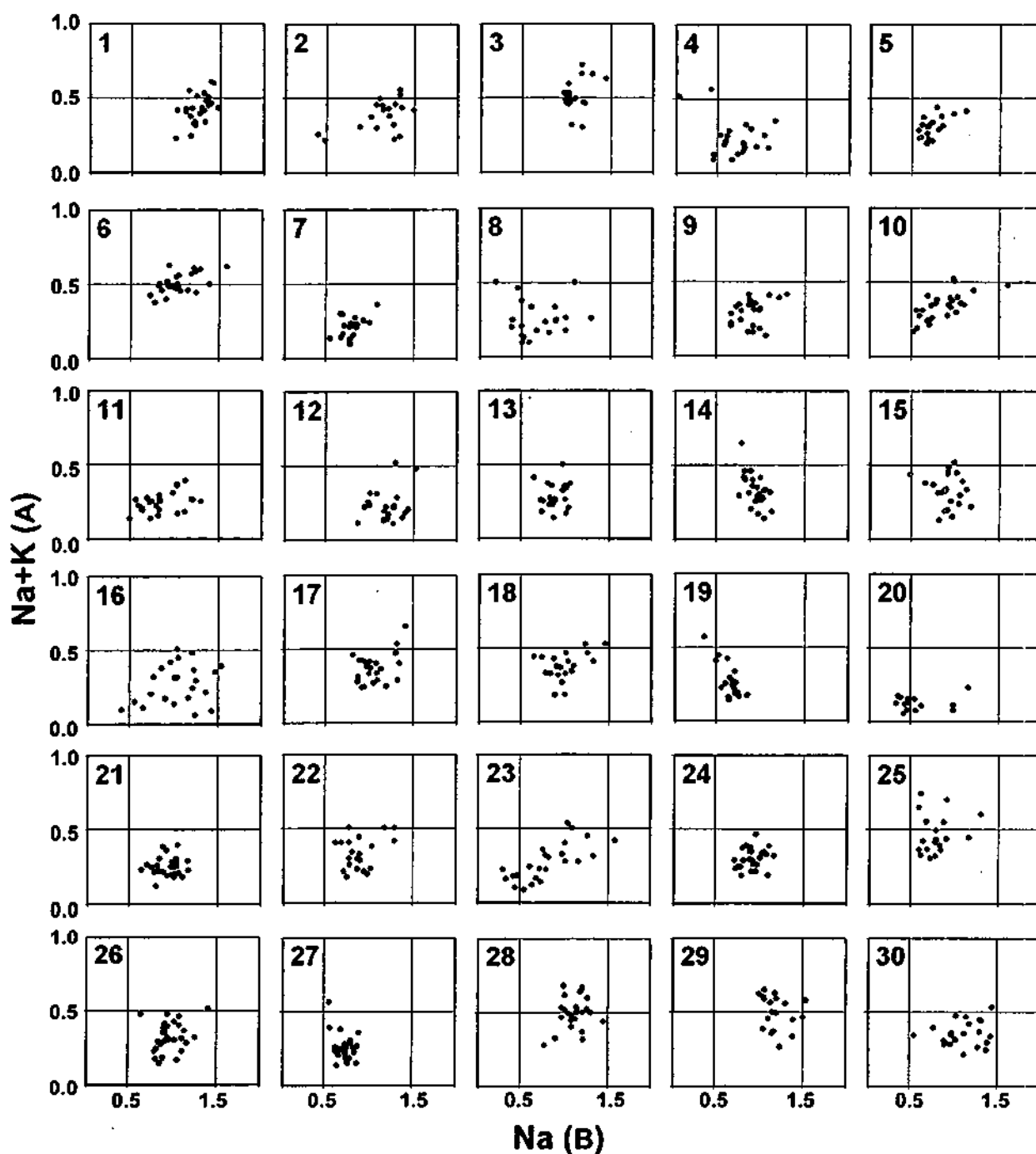
FIGURE 7. EDS data for 30 samples showing the distribution of compositions of the fibrous and friable amphibole for each sample location at the mine (see Fig. 1). Sample number is in the top left corner of each plot (see Fig. 1). Mineral fields are the same as shown in Figure 6.

The data shown in Figure 11 are plotted as diameter vs. length and diameter vs. aspect ratio, respectively. These data, which were obtained from samples 4, 10, 16, 20, and 30, represent the range of amphibole compositions sampled. For the most part, all of the samples produce fibers in a similar size range. It is important to remember that these samples were not ground to produce these particles. The fibers were collected on the SEM stubs by touching the stub to the inside of the original sample bag after it was received from the field and other sample material was removed. Approximately 40% of the particles are greater than 5 µm in length and have aspect ratios greater than 3. This finding means that, based on size, these particles are countable as asbestos by most approved methods such as Crane (1992). Even if more conservative counting criteria are employed, such as ≤0.5 µm diameter with aspect ratios of ≥10, approximately 30% of the particles would be included. These observations dem-

FIGURE 9. Back-scattered electron image of an area of a thin section of sample 24 showing massive and fibrous amphibole (Amp) intergrown with secondary calcite (Cal), titanite (Ttn), and quartz (Qtz). Note the fibrous amphibole enclosed by the large titanite grain at lower right, indicating order of crystallization.

FIGURE 8. Transmitted-light images of entire polished thin sections showing: (a) amphibole filling a vein with symmetric dark and light (center of the vein) layers and (b) amphibole (dark areas) replacing pyroxene crystals. (c) A large single pyroxene crystal (bright areas) partly replaced by amphibole (dark areas) along crystallographically oriented planes is shown in transmitted, cross polarized light.

onstrate that the Vermiculite Mountain amphiboles, with minimal disturbance, can easily degrade into highly acicular particles that are less than 3 μm in diameter and are therefore respirable (National Academy of Sciences 1984).

DISCUSSION

The amphibole samples analyzed in this study show a large range in chemical composition. This range is consistent with varying degrees of, and possibly different episodes of, alteration of the original pyroxenite body by hydrothermal fluids associated with the intrusion of syenite and related rocks. The

variations in composition seen in the EDS data in Figure 7 do not appear to correlate directly with sample location. Samples 5, 6, and 7 were collected in close proximity to each other. Samples 5 and 7 show a similar compositional distribution, but the compositions in Sample 6 are distinctly different. Sample pairs 4 and 28, and 27 and 29 were collected from locations that are relatively close to each other and well within the biotite pyroxenite. Both of these show distinctly different amphibole compositions within each pair. These data suggest that the compositional differences are not due to location or gross zoning within the intrusion. The variations are more likely due to the reaction of pyroxene with different compositions of hydrothermal fluids associated with the quartz-rich veins and the trachyte, phonolite, and syenite dikes described by Boettcher (1966b, 1967). The variations also could be due to differences in the duration of fluid-rock interaction.

In addition to compositional variations among samples, EPMA data show compositional variations on the micrometer scale. Several samples showed changes in the amphibole mineral within single grains or fiber structures. Figure 12a shows a non-fibrous amphibole crystal with concentric zoning from magnesioriebeckite in the core to winchite at the rim. Figure 12b shows a single amphibole grain with compositions ranging from tremolite to winchite.

The variability of compositions on the micrometer scale can produce single fibrous particles that can have different amphibole names at different points of the particle. This type of variation has implications for the regulatory community. Morphologically, such structures might be considered fibers by most analytical protocols (Crane 1992, 1997; Baron 1994). However, by some current regulations and approved analytical methods, the variable chemistry of these particles could exclude them from being classified as "asbestos." This complexity creates a dilemma for the analyst who is charged with determining
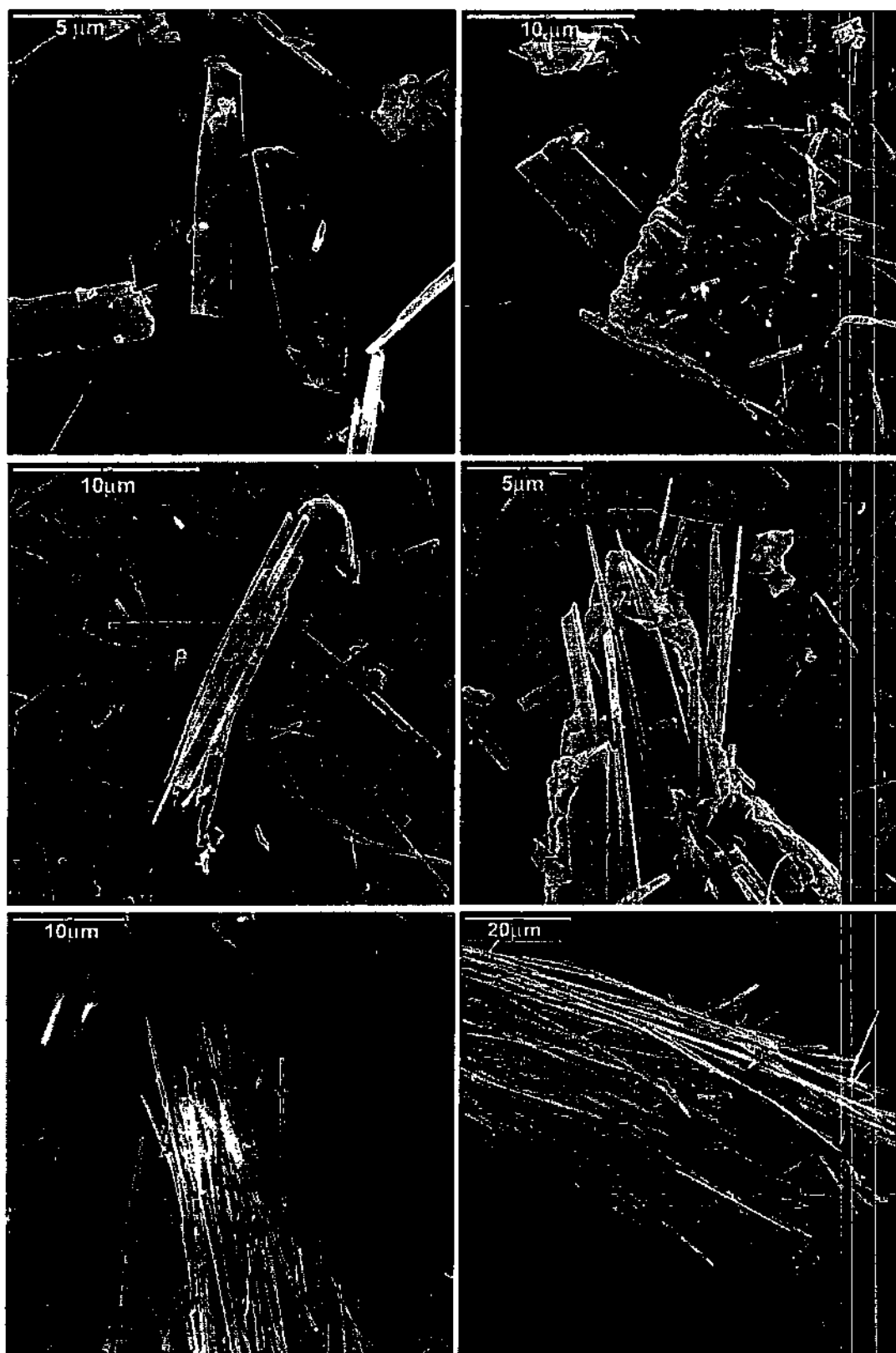
FIGURE 10. Electron micrographs of typical morphological types of Vermiculite Mountain amphiboles. The morphologies range from prismatic crystals (upper left) to long fibers and bundles (lower right).
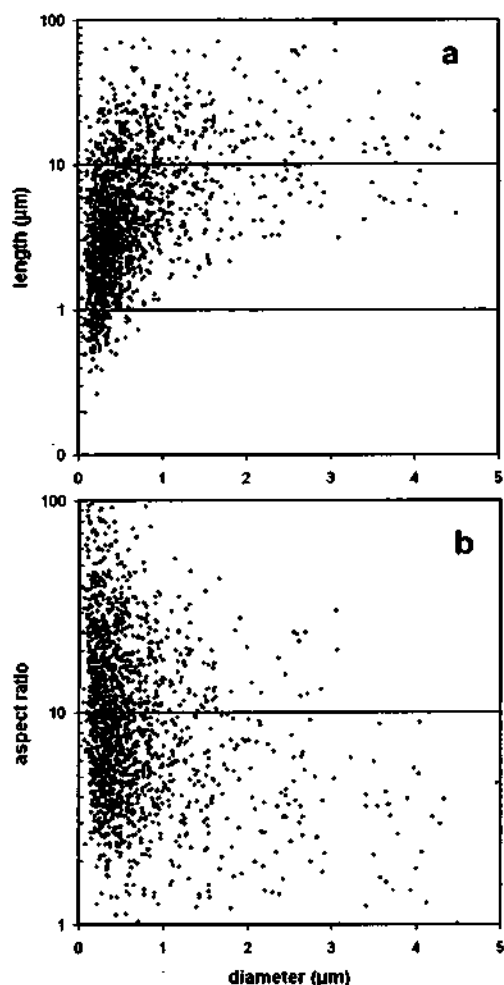
FIGURE 11. Amphibole particle size data from samples 4, 10, 16, 20, and 30 for particle diameters 5 μm and less, plotted as length vs. diameter (a) and aspect ratio (length:diameter) versus diameter (b).

whether asbestos is present in a sample and at what level.

A further dilemma arises from the fact that none of the present regulatory analytical methods (with the possible exception of well-calibrated SEM/EDS analysis using calibration standards similar to EPMA/WDS) can accurately differentiate the amphiboles present in the asbestiform materials from Vermiculite Mountain. Even with standard optical techniques, the results can be ambiguous (Wylie and Verkouteren 2000). This ambiguity arises because the mineralogical community currently classifies amphiboles on the basis of crystal chemistry, and high precision and accuracy in the microanalytical technique employed are required to classify an amphibole accurately. Analytical electron microscopy (TEM/EDS) provides compositional information, but the thickness of the sample must be known to provide accurate chemistry. This information is normally not available during routine TEM analysis of asbestos fibers as would be performed when following approved asbestos analysis methods such as ISO 10312 (1995).

The problem of classification is complicated further when the oxidation state of Fe is considered. This complication is illustrated in Figure 3, where the amphibole-species distribution is seen to shift significantly when the analyses are calculated using pure Fe^{+2} and Fe^{+3} end-members. The degree of accuracy and precision required to determine the correct oxidation state of Fe is not achievable during routine microanalysis of small, unpolished, single structures by SEM/EDS or TEM/EDS. Therefore, any regulatory distinction between minerals that requires knowledge of the oxidation state of Fe, such as the distinction between tremolite and actinolite, is technically not possible without a full quantitative chemical analysis.

Our analysis of unpolished, micrometer-sized particles of a basalt glass standard by SEM/EDS resulted in the 2σ errors as high as ±25% relative for Na and ±14% for Fe. Without the ability to correlate unpolished single-fiber SEM/EDS analyses with EPMA data from polished samples, it would be extremely difficult to confirm the presence of any of the amphibole min-
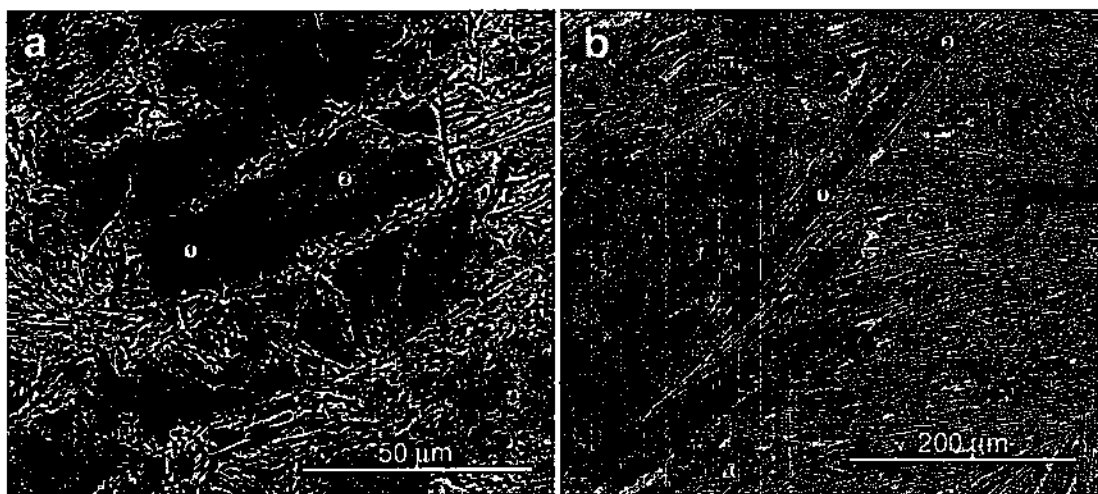
FIGURE 12. (a) Back-scattered electron image showing a prismatic amphibole grain with a rim of winchite (point 1) and a core of magnesioriebeckite (point 2), partially surrounded by fibrous amphibole. Other grains of similar composition can be seen above and below. (b) Backscattered electron image showing a large single amphibole structure (center) exhibiting fibrous habit at the ends and along the margins. Point 1 is tremolite and point 2 is winchite.

erals identified in this study by EDS alone. We therefore recommend that the International Mineralogical Association classification system (Leake et al. 1997) for amphiboles not be used for regulatory purposes in cases where high analytical precision and accuracy cannot be demonstrated.

If a microanalytical technique does not have the precision and accuracy to classify amphibole asbestos correctly according to current mineralogical criteria, then how should asbestos, such as that found at Vermiculite Mountain, be classified? Within much of the existing asbestos literature, mineral names are not applied in a uniform manner and are not all consistent with presently accepted mineralogical nomenclature and definitions. Tremolite and actinolite (members of the solid-solution series tremolite-ferroactinolite), and anthophyllite are mineral names recognized by the Subcommittee on Amphiboles of the International Mineralogical Association (Leake et al. 1997). For these three amphibole species, the term "asbestiform" usually must precede the mineral name, or the term asbestos must be added after the mineral name to denote a regulated material. The name amosite, derived from an acronym for Asbestos Mines of South Africa, is generally considered to refer to the asbestiform varieties of minerals in the cummingtonite-grunerite solid-solution series (Rabbitt 1948; Vermas 1952; Bowles 1959). Crocidolite is the asbestiform variety of the amphibole riebeckite. This inconsistency in the application of nomenclature can cause significant problems for asbestos analysts, medical professionals, and regulators who are unfamiliar with the principles of mineralogic classification, including solid-solution. In addition to the five amphibole asbestos "minerals" normally cited in the regulatory literature, many other amphibole minerals have been reported to occur in asbestiform and fibrous habit (Zoltai 1981; Wylie and Huggins 1980). A few methods and regulations (e.g., ISO 10312, method for TEM analysis of asbestos) recognize the possible existence of other asbestiform amphiboles, but make no attempt to identify or define them mineralogically.

To complicate further the problems in nomenclature cited above, the nuances of mineralogical classification systems are often not specified or are not well defined in the regulatory literature for many potentially fibrous and asbestiform amphiboles (Lowers and Meeker 2002). In many cases, nominal compositions are given for a mineral but no chemical boundaries are specified. Furthermore, the techniques and methods available and approved for the analysis and classification of asbestos by regulatory entities are often not capable of adequately identifying or distinguishing many of these minerals according to current mineralogical guidelines (such as Leake et al. 1997). This problem is particularly true for microanalytical techniques such as TEM and SEM employing qualitative or semiquantitative EDS.

By virtue of the age of regulatory documents, the current regulatory language (i.e., Bridbord 1976; OSHA 1992) omits richterite and winchite. A better alternative for regulatory nomenclature, consistent with modern mineralogical terminology and analytical capabilities, would be to replace the names of the five amphiboles, tremolite asbestos, actinolite asbestos, crocidolite, amosite, and anthophyllite asbestos by the term "asbestiform amphibole" as suggested by Wylie and

Verkouteren (2000) or by "fibrous amphibole," if such a description is deemed necessary by the medical and health science community. Barring any such changes in the current regulatory language, the Vermiculite Mountain amphibole asbestos could, for the purposes of regulation only, be considered equivalent to tremolite or soda-tremolite asbestos in accordance with current and past industrial terminology for the Vermiculite Mountain amphiboles.

In addition to chemistry, morphology is a primary factor in evaluation of the asbestiform and fibrous amphiboles. Nomenclature is again a key issue in a discussion of morphological characteristics of amphiboles, particularly those from Vermiculite Mountain. Amphiboles can occur in fibrous and non-fibrous forms. Fibrous amphiboles can further be classified as asbestiform and non-asbestiform. The term asbestiform is usually applied to populations of single-crystal fibrils (the smallest structural unit of a fiber), which occur in bundles and possess certain characteristics including high aspect ratio, high tensile strength, and flexibility (Zoltai 1981; Perkins and Harvey 1993; Wylie 2000). Another class of amphibole particles, cleavage fragments, can exist in blocky or acicular habit. Regardless of aspect ratio, cleavage fragments are formed by the breaking of a larger crystal. Interestingly, Ahn and Bueck (1991) have described asbestiform riebeckite from Western Australia that appears to have formed by the separating or breaking of larger crystals on dislocation planes of weakness along (100) and (110). A similar formation mechanism was proposed by Veblen (1980) for a sample of asbestiform anthophyllite. These findings obscure somewhat the traditional definition of asbestiform. The Vermiculite Mountain amphiboles serve to underscore the fact that traditional morphological definitions of asbestos may not adequately define amphibole mineral fibers from a toxicological and regulatory perspective.

Within the asbestiform amphibole minerals median diameters vary. Veblen and Wylie (1993) presented data suggesting that tremolite asbestos and anthophyllite asbestos fibers have larger diameters (median about 0.45 μm), and riebeckite asbestos fibers have smaller diameters (median about 0.2 μm). Byssolite is a term that is sometimes applied to single acicular amphibole crystals with an average diameter of about 1–2 μm (Veblen and Wylie 1993) or "often wider than 1 μm" (Wylie 1979). Our data show the median diameter of the respirable fibrous component (less than 3 μm in diameter) of five Vermiculite Mountain amphibole samples to be 0.44 μm. The average diameter for the same set of particles is 0.56 ± 0.45 μm (1σ). From these data, the diameter of the Vermiculite Mountain amphiboles appears to be at the upper range for asbestos and overlaps with the size range cited for byssolite.

Cleavage fragments were specifically excluded from material regulated by OSHA in 1992 (OSHA 1992). Therefore, regardless of any mineralogical, physical, or toxicological differences that might exist among acicular cleavage fragments, byssolite, and asbestiform fibers, differentiation among these classes of particles has become an issue. With the amphiboles, the morphologic distinction between asbestiform fibers and cleavage fragments can be made readily in many cases. This distinction is particularly true when "high-grade" asbestos of commercial value is being compared to blocky cleavage frag-

ments generated by grinding an amphibole such as massive tremolite. The distinction is not as clear when non-commercial-grade fibrous amphiboles, like those from Vermiculite Mountain, are being evaluated. For example, by some definitions (e.g., Perkins and Harvey 1993; Wylie 2000), a population of "true" asbestos fibers should have a minimum mean aspect ratio of 20 for individual fibers longer than 5 μm. In our size analysis of five of the Vermiculite Mountain samples plotted in Figure 11, three samples had mean aspect ratios slightly higher than 20 whereas two had mean aspect ratios slightly lower. The mean aspect ratio for all five samples, for fibers longer than 5 μm, was only 22. The task of distinguishing between what traditionally has been considered asbestos from byssolite and cleavage fragments can become much more difficult if not impossible when only single amphibole particles are being evaluated, and a representative population of the amphibole material is not present. Such a situation can be encountered in the analysis of environmental samples of air, soil, or water.

The Vermiculite Mountain amphiboles display characteristics that include all of the above morphological classes in a continuum, from blocky crystals to acicular, non-flexible cleavage fragments, to extremely long flexible fiber bundles (Fig. 10). Most of the individual particles display features that are intermediate between cleavage fragments and long flexible fibers. There are no distinct morphological boundaries by which to categorize the amphiboles. In addition, the mineralogy of these amphiboles is not typical of most regulated asbestos. Given the variations and ambiguities in much of the morphological and mineralogical terminology expressed in the mineralogical, medical, industrial, and regulatory literature (Lowers and Meeker 2002), the Vermiculite Mountain amphiboles present a significant challenge to the analyst, to anyone attempting to classify the material with respect to existing definitions, and particularly to those attempting to extrapolate those morphological features and chemical compositions to potential toxicological properties.

ACKNOWLEDGMENTS

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A BASALT GLASS STANDARD FOR MULTIPLE MICROANALYTICAL TECHNIQUES

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Well-characterized calibration standards for microanalytical applications are difficult to obtain, often poorly characterized, and often not homogeneous from piece to piece. In addition, many microanalytical standards are available only in very small quantities making inter-laboratory comparisons difficult. To further complicate the situation, destructive microbeam techniques such as secondary ion mass spectrometry (SIMS) and laser source mass spectrometries (LSMS) require larger quantities of material than nondestructive techniques.

The U.S. Geological Survey, Geologic Division is in the process of evaluating ways to produce relatively large quantities of well-characterized standards. We are interested in producing standards of geological materials appropriate for multiple microbeam techniques including electron probe microanalysis (EPMA), SIMS and LSMS.[1] The microbeam standards are produced by melting powders of standards of naturally occurring materials that the USGS has previously provided as bulk analytical standards. Our criteria for the microbeam standards are: 1) the composition of the standard is accurately determined by a variety of techniques, 2) the standard is homogeneous on a micrometer scale, 3) sufficient material (i.e. several hundred grams) is available for a large number of laboratories to maintain a supply for use into the foreseeable future, 4) the standard contains a large number of elements of interest to the geologic community, and 5) the standard is stable during storage and analysis.

We have produced approximately 400 grams of a basalt glass microbeam standard that appears to meet all of the criteria above. The standard has been distributed previously in powder form as BIR1, for use with bulk analytical techniques.[2] Our microbeam glass standard was produced by melting BIR-1 powder in a Pt crucible in a furnace with a nitrogen atmosphere. The material was stirred several times during the melting process with a Pt rod to insure homogenization. The molten material was poured into a Pt boat bathed in nitrogen gas, and floating in a tank of water. Polished thin sections of randomly selected chips of the standard were examined optically, by backscattered electron imaging; and by EPMA for homogeneity and composition.

Optical examination using reflected and transmitted light revealed no crystallites or precipitates. Backscattered electron imaging of the sample revealed no compositional variation in any of 10 randomly selected chips. EPMA analyses were performed in two modes. In the first set of analyses five wavelength spectrometers were set to peak positions for Si, Al, Mg, Fe, and Ti. Traverses were made without moving the spectrometers for background measurements (Table 1). The second set of analyses was performed in the conventional mode using background measurements (Tables 2 and 3). X-ray fluorescence data has been obtained from powdered chips of the glass material (Table 2).

The results of these analyses indicate that this standard is suitable for general distribution as an electron microbeam standard. A round-robin EPMA study of the standard is presently being conducted to help determine the nominal major and minor element values for the material. Further analyses by other techniques are also underway to refine nominal major, minor and trace element

values. This microanalytical basalt glass standard will be called BIR-1-G and will be available for general distribution after the round-robin and other analyses are complete.

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Table 1. EPMA raw count data from 481 points obtained without moving spectrometers (15kV, 33nA, 10 μm spot). Si (static) acquired on a single spot.

	A vg. Counts	Std. Dev. (1σ)
Si	410593	2387
Al	99367	690
Mg	65649	462
Fe	38903	242
Ti	6048	76
Si (static, 50 analyses)	412755	897

Table 2. Average weight percent oxide from 274 points determined by EPMA at 15kV, 20nA with a 10 μm spot size. CITZAF matrix corrections were used. Also shown are EPMA standards used, XRF data from powdered glass chips, and bulk composition of starting material material.

	A vg. Wt% EPMA*	Std. Dev. (1 σ)	EPMA Standard	XRF Analysis* Powdered Glass	Bulk Composition Starting Material[2]
Na_2O	1.82	0.03	I jadite	1.71	1.75
MgO	9.78	0.13	diopside	9.53	9.68
Al_2O_3	15.6	0.13	anorthite	15.4	15.35
SiO_2	47.9	0.23	orthoclase	47.3	47.77
K_2O	0.04	0.01	orthoclase	0.04	0.03
CaO	13.3	0.16	anorthite	13.1	13.24
TiO_2	0.94	0.03	TiO_2 (syn)	0.96	0.96
MnO	0.17	0.02	spessartine	0.17	0.17
FeO	10.1	0.20	Fayalite (syn)	10.0	10.13
Total	99.67	0.38			

Table 3. Results from 5 different traverses (T1-T5), on different chips, of data summarized in Table 2. Analysis points approximately 50 μm apart. 1σ error given in parentheses. EPMA analysis conditions same as Table 2.

	T1 (75 pts.)	T2 (50 pts.)	T3 (53 pts)	T4 (47pts.)	T5 -(45 pts.)
Na_2O	1.84 (.03)	1.83 (.04)	1.83 (.04)	1.80 (.03)	1.80 (.03)
MgO	9.78 (.14)	9.73 (.15)	9.78 (.14)	9.79 (.11)	9.79 (.13)
Al_2O_3	15.6 (.12)	15.6 (.16)	15.6 (.12)	15.6 (.12)	15.6 (.12)
SiO_2	47.9 (.22)	47.8 (.31)	47.9 (.21)	47.8 (.23)	47.8 (.28)
CaO	13.2 (.18)	13.3 (.12)	13.3 (.19)	13.2 (.15)	13.2 (.17)
TiO_2	0.94 (.03)	0.94 (.03)	0.95 (.03)	0.94 (.02)	0.94 (.03)
MnO	0.17 (.02)	0.17 (.02)	0.17 (.02)	0.17 (.02)	0.17 (.02)
FeO	10.2 (.20)	10.1 (.18)	10.1 (.20)	10.1 (.22)	10.1 (.22)

* These numbers are preliminary and not to be considered as the final recommended values.

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NMAM is a collection of methods for sampling and analysis of contaminants in workplace air, and in the blood and urine of workers who are occupationally exposed. These methods have been developed or adapted by NIOSH or its partners and have been evaluated according to established experimental protocols and performance criteria. NMAM also includes chapters on quality assurance, sampling, portable instrumentation, etc.

Complete document is available at www.cdc.gov/niosh/nmam

L.   MEASUREMENT OF FIBERS
by Paul A. Baron, Ph.D., NIOSH/DART

Adapted from Baron [1]

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1.   INTRODUCTION

Fiber-related disease has provided much of the impetus for fiber research in recent years. Asbestos has been the fiber type most commonly associated with disease. The name "asbestos" is a commercial term applied to the fibrous forms of several minerals that have been used for similar purposes and includes chrysotile, amosite, crocidolite, and the fibrous forms of tremolite, anthophyllite, and actinolite. The three primary diseases associated with asbestos exposure are asbestosis, the result of inflammation and collagen formation in lung tissue; lung cancer; and mesothelioma, an otherwise rare form of cancer associated with the lining surrounding the lungs. A current theory describing the toxicity of fibers indicates that fiber dose, fiber dimension, and fiber durability in lung fluid are the three primary factors determining fiber toxicity [2].

The dose, or number of fibers deposited in the lungs, is clearly an important factor in determining the likelihood of disease. Both fiber diameter and length are important in the deposition of fibers in the lungs and how long they are likely to remain in the lungs. Figure 1 indicates some of the factors that determine fiber deposition and removal in the lungs. Fiber length is thought to be important because the macrophages that normally remove particles from the lungs cannot engulf fibers having lengths greater than the macrophage diameter.

Thus, longer fibers are more likely to remain in the lungs for an extended period of time. The macrophages die in the process of trying to engulf the fibers and release inflammatory cytokines and other chemicals into the lungs [3]. This and other cellular interactions with the fibers appear to trigger the collagen buildup in the lungs known as fibrosis or asbestosis and, over a longer period, produce cancer as well. Fiber diameter is also important because fiber aerodynamic behavior indicates that only small diameter fibers are likely to reach into and deposit in the airways of the lungs. The smaller the fiber diameter, the greater its likelihood of reaching the gas exchange regions. Finally, fibers that dissolve in lung fluid in a matter of weeks or months, such as certain glass fibers, appear to be somewhat less toxic than more insoluble fibers. The surface properties of fibers are also thought to have an effect on toxicity. Asbestos is one of the most widely studied toxic materials and there have been many symposia dedicated to and reviews of its behavior in humans and animals [4-8].

Several techniques were used for asbestos measurement up until the late 1960s [8]. Earlier than this, it was not widely recognized that the fibrous nature of asbestos was intimately related to its toxicity, so many techniques involved collection of airborne particles and counting all large particles at low magnification by optical microscopy. Thermal precipitators, impactors (konimeters), impingers, and electrostatic precipitators were all used to sample asbestos. Perhaps the primary technique in the United States (US) and the United Kingdom (UK) during this early period was the liquid impinger, in which particles of dust larger than about 1-µm aerodynamic diameter were sampled at 2.7 L/min and impacted into a liquid reservoir [8]. After sampling, an aliquot of the liquid was placed on a slide in a special cell, particles larger than 5-µm size were counted, and the results were reported in millions of particles per cubic foot. Dissatisfaction with this approach stemmed from lack of correlation between measured particle concentration and disease in the workplace. Various indices of exposure have been developed that attempt to relate a portion of the fiber size distribution to the toxic effects. The appropriate indices for each of the asbestos related diseases as a function of fiber length and diameter (Figure 2) were suggested by Lippmann [9].

2. FIBER DIMENSIONS

Fibers are particles that have one dimension significantly larger than the other two. Fibers are often characterized or selected according to their aspect ratio, i.e., the ratio of the large dimension to one of the small dimensions. If no other criteria are used, then materials that might not normally be considered fibrous may contain a fraction of particles that meet the criteria for fibers. The distribution of fiber dimensions in a sample can usually be characterized by assuming a cylindrical geometry (i.e., the two small dimensions are identical) and measuring the length and diameter of individual fibers. The distribution of airborne fiber sizes generated by grinding bulk material or by mechanically releasing particles into the air often results in a two-dimensional (bivariate) lognormal distribution. Such a distribution is characterized by five parameters: the geometric mean length, the geometric mean diameter, the length and diameter geometric standard deviations, and a correlation term that relates length to diameter [10]. In addition, several other parameters that are a function of length and diameter, such as aerodynamic diameter, can also be characterized by a lognormal distribution [11].

Often the discussion of fibers assumes that fibers are straight objects that can be well defined by several parameters as indicated above. However, many real-world particles are not so simple to describe. In fact, the detailed features of many fibers can aid in their identification [12]. Fibers are often curved, have splayed ends, or differ in other ways from a cylindrical shape. Asbestos mineral is composed of fibrils (about 0.03-µm diameter) that are packed together. This fibrillar structure is characteristic of asbestiform minerals. When the mineral is broken apart mechanically, the material separates primarily between fibrils and the resulting fibers are usually bundles of fibrils. The ends of the fibers can be broken apart, with smaller bundles or individual fibrils spread apart, yet still be part of the fiber. Fibers can be contaminated by attachment of other dust particles, creating a complex structure with aerodynamic behavior not matching that of cylindrical fibers. The complexity of fiber shapes affects all of the measurement and separation techniques described below and frequently makes it difficult to compare one method to another.

In addition to asbestos fibers, there are many types of fibrous materials being produced for commercial purposes. These include fibrous glass, mineral wool, refractory ceramic fibers, wood and other plant fibers, and synthetic organic fibers. Most of these fibers tend to have larger diameters than asbestos fibers. On the other hand, carbon nanotubes (<0.005-µm diameter) have recently been produced in small-scale commercial quantities and because of their high tensile strength, high conductivity, and other special properties, show great promise as a commercial material [13]. Measurement techniques must be tailored to the size distribution and physicochemical properties of the fibers.

This review primarily relates to measurement of fibers in air. There are a several techniques that address concentration of asbestos and other fibers in bulk material and measurement of mass concentration of fibers [14]. One of these bulk methods, polarizing light microscopy, will be discussed below.

3. PHASE CONTRASTING LIGHT MICROSCOPE COUNTING (PCM)

As asbestos-induced disease became widely studied in the 1960s, cellulose-based membrane filter sampling was applied to asbestos sampling in combination with high magnification phase contrast light microscopy (PCM) for counting fibers. This technique involved collection of fibers uniformly over the surface of a cellulose ester filter, placing the filter or a segment of the filter on a microscope slide and making it transparent, and observing the fibers in the sample with a high magnification (~450X) phase contrast light microscope. Over the years, many researchers have endeavored to improve and standardize the PCM method. One researcher, Walton, discussed many aspects of this technique in a review [15]. The high variability of the analysis results and the method's dependence on operator technique made method improvement and research difficult. The PCM method does not measure all fibers; typically only those >0.25-µm diameter are visible and counted and only those >5 µm length are counted by protocol. Therefore, the PCM method is only an index of exposure and uses the assumption that what is detected is correlated with the fibers actually causing disease (Figure 2). The PCM method does not allow identification of asbestos fibers. This is an important limitation when the method is used in settings where fiber concentrations with a significant non-asbestos fraction may occur. This should be remembered when considering some of the parameters discussed below. The aim of evaluating changes to the PCM technique may depend on whether consistency with other

laboratories within a country or throughout the world is more important than making measurements that are more closely related to health effects. A number of factors which influence analysis results have been investigated, including the following.

a. Microscope-related parameters

Microscope magnification. The exact level of microscope magnification depends on microscope design, but most current methods use 450X (±10%) total magnification. Pang and coworkers investigated 1250X magnification to improve fiber detectability, but this has not been adopted in any established methods [16]. Pang also investigated the effect of using lower magnification (400X) and found that counts were lower for chrysotile asbestos by 25%, but that amosite fiber counts were unaffected [17].

Phase contrast optics. This contrast enhancement technique allows detection of asbestos fibers down to about 0.25 µm diameter for chrysotile and about 0.15-µm for amphiboles. Other techniques such as dark field microscopy may offer improved detectability, but also increase the background from non-fibrous particles.

Test slide to check optics. A test slide was developed to allow a check of proper alignment and magnification in the microscope [18]. This ensures a reasonable level of uniformity in microscope setup and operation, including the operator's visual perception. Improper setup can reduce detectability of fibers. There have also been cases where the optics were "too good," and results were obtained that were higher than the reference count.

Counting area in microscope field. Some early measurements with the phase contrast microscope were made using a rectangular graticule for defining the counting area, while others were made using the entire microscope viewing area. It was found that larger viewing areas resulted in lower counts, so the Walton-Beckett graticule [19] was developed that nominally gave a 100-µm diameter counting area (the area is calibrated more precisely for each microscope) and has been incorporated in all current methods.

b. Sample preparation techniques

Filter type. Virtually all measurements are made using 0.8-µm pore size mixed cellulose ester (MCE) filters. Some measurements are made using 1.2-µm pore size filters when sampling low concentrations to allow higher flow rate through the filter. Smaller pore size filters are used to ensure that fibers are deposited as near the surface of the filters as possible. This results in fibers ending up in the same plane so that they can be readily viewed with a minimum change of focus during fiber counting. Pore sizes smaller than 0.8 µm are only used with line-operated pumps because of limited suction power available with personal sampling pumps.

Selection of the liquid for making filter transparent. A liquid is placed on the filter that closely matches the filter refractive index, yet has an index that is as far as possible from that of the fibers being detected. Rooker et al. showed that refractive index difference between cleared filter and fibers translated directly into detectability of small diameter fibers [20]. A viscous solution of dimethyl phthalate and diethyl oxalate mixed with cellulose filter material was commonly used in the 1970s and early 1980s. However, it did not result in a permanent

sample, with crystallization of the mount and movement of fibers often occurring several days after sample preparation. Permanent slides were needed for quality assurance purposes and the sample preparation technique was also slow and required some skill. A rapid acetone-based filter clearing technique was developed that could be used safely in field situations [21]. After clearing, filters were coated with triacetin to surround the fibers. This resulted in a longer lasting sample (typically months to years) and is currently specified in most methods. Another technique uses a resin called Euparal to surround the fibers and results in a permanent slide preparation [22].

Filter loading. The number of fibers on the filter is usually specified to be within a certain loading range to ensure consistent counting. Cherrie *et al.* demonstrated using a serial dilution technique that counting efficiency was a function of concentration of fibers on the filter [23]. At very low filter loadings (<100 fibers/mm^2) there was a tendency to count high relative to an intermediate range of concentrations (100-1300 fibers/mm^2), where the counts were a linear function of loading. This "overcounting" was apparently due to greater visibility of fibers in a clean visual field. This effect was noted for both human counters and an image analysis system. At high filter loadings (>1300 fibers/mm^2), undercounting occurred due to overlap of fibers with other fibers and with nonfibrous particles. Most published methods indicate that optimum counting occurs within the 100-1300 fibers/mm^2 range, while some restrict the range further to less than 650 fibers/mm^2.

Fiber counting rules. The basic fiber counting rules for most current methods indicate that a countable fiber should be longer than 5 µm, narrower than 3 µm, and have an aspect ratio greater than 3:1. These rules were selected because shorter fibers were difficult to detect by optical microscopy and the 3:1 aspect ratio was used to discriminate between fibrous and non-fibrous particles in occupational settings. There has been a great deal of controversy over these rules. The use of a longer fiber cutoff, e.g., 15   20 µm, has been suggested, based on two separate arguments: first, that most asbestos fibers are relatively long and thin (with high aspect ratio) and the longer fiber cutoff would discriminate better toward fibers that were truly asbestos fibers according to mineralogical definitions [24]; and second, that fibers that enter the lungs are removed readily by macrophages if they are shorter than about 15 µm [3]. Longer fibers cannot readily be engulfed by macrophages, thus staying in the lungs for a long period and causing continuing fibrosis.

The aspect ratio criterion has also been questioned because many non-asbestiform particles have shape distributions that include particles with aspect ratios greater than 3:1. Since asbestos and other minerals often contain single crystal particles not in the asbestiform habit, it has been argued that these single crystals, or cleavage fragments, should not be counted. However, the Occupational Health and Safety Administration (OHSA) has supported the 3:1 minimum aspect ratio through legal precedent. The National Institute for Occupational Safety and Health (NIOSH) has noted that because of the great difficulty in differentiating whether individual high aspect ratio particles are cleavage fragments or asbestiform fibers, all such particles should be counted. These high aspect ratio particles may cause disease whether or not they are asbestiform.

Other aspects of fiber counting have been investigated, including how to count non-standard fiber shapes, overlapping fibers, overlapping compact particles on fibers, and bundles of fibers. Each of these factors can have a noticeable effect on the final count. Cowie and

Crawford investigated the effect of some of these factors and estimated most of them made a difference in the final count on the order of 20% [25]. Many of the methods currently in use have slight variations in their interpretation of which fibers to count and thus can contribute to variation in results between countries and organizations.

NIOSH Method 7400 contains two sets of counting rules, the A and the B rules. The A rules are used for asbestos and are consistent with counting rules in previous NIOSH methods. The A rules are required for asbestos counting by OSHA because of legal precedent in regard to the 3:1 aspect ratio rule. The A rules do not have an upper diameter limit for fibers to be counted. The B rules were introduced as an alternative to the A rules when Cowie and Crawford found that these rules agreed best with previous PCM counts, yet had improved precision [25]. The B rules have been informally adopted for use with fibers other than asbestos because these rules include the upper diameter limit of 3 µm. This upper diameter limit significantly reduces the counting of typically large-diameter fibers, e.g., glass and cellulose, that are unlikely to deposit in the lungs [26].

c. **Quality assurance schemes**

Sample recounts. Most methods require individual counters to recount about 10% of the field samples to ensure consistent counting procedures and alert the analyst in the case of problem samples. It is also recommended that counters have samples that are routinely recounted to ensure consistent counting within a laboratory over time.

One of the difficulties in analyzing errors made by analysts during PCM counting is that individual fields are difficult to relocate after the analyst has finished counting a slide. Differences in counts between analysts have often been ascribed to local variations in loading on the filter. Pang's development of a slide coverslip that defines counting areas on the sample solves this problem [17]. Areas on the coverslip are vacuum coated with a thin layer of gold and platinum using an electron microscope grid as a mask. This leaves defined areas on the coverslip that can be located by grid index marks. Thus, specific fields in a sample can be readily located. Using this grid mapping approach, the location, orientation and shape of each fiber can be noted and differences in counts can be reconciled on a fiber-by-fiber basis. The coverslips have been used to study fiber counting accuracy by comparing routine counting of specified fields to counts agreed upon by a group of competent counters. It was found that the principal errors for chrysotile fiber samples were due to missing fibers close to the visibility limit, while the principal errors for amosite fiber samples were caused by incorrectly sizing fiber length near the 5-µm limit. The chrysotile samples were therefore typically undercounted (negative bias), while the amosite samples had increased variability with individual counters being biased either high or low. Both these errors can be reduced by training counters with pre-counted reference slides prepared using Pang's coverslips [17] (Omega Specialty Instrument Co. Chelmsford MA). In addition, these reference slides can be used on a routine basis to ensure consistency in counting. These coverslips or modified versions show great promise for training analysts and perhaps for improving quality assurance schemes.

Interlaboratory sample exchanges. Crawford *et al.* found that use of sample exchange programs was more important in ensuring agreement between laboratories than similarity in details of the counting rules [27]. Thus, exchange of field samples between laboratories is

commonly performed to improve consistency of counting. A description of several quality assurance techniques for asbestos fiber counting is described by Abell *et al* [28]. To fulfill Method 7400 requirements for an interlaboratory sample exchange, Tombes and Calpin have described a simple approach using appropriate statistical tests [29].

Quality check samples. In order to get agreement between laboratories within a country or internationally, several programs send out identical samples to participating laboratories to assess their relative performance [30-33]. These programs provide feedback, often tied to laboratory accreditation, which provides incentive for laboratories to ensure that their performance is similar to that of other laboratories.

d. Qualitative fiber analysis

In addition to simply counting the fibers, there are techniques available for providing at least tentative identification of fiber type; use of these techniques is commonly called differential counting. Fiber shape can be used to limit the type of fiber counted. For instance, glass fibers tend to be straighter, with smoother sides than chrysotile fibers. Polarizing light techniques can also be used to identify larger diameter ($> 1 \mu m$) fibers. These are based on the optical properties of the materials, including refractive index and crystallinity. These techniques can provide quite positive identification for the presence of certain types of fibers, but are limited in application to airborne fibers because they only work for the larger diameter fibers. These techniques are often used in analysis of bulk materials [34]. The use of identification techniques is not allowed in reporting fiber counts using Method 7400 so that the results are consistent between laboratories. Considerable confusion has been caused in the past by individual laboratories using some of these identification techniques to change the counting procedure and, hence, the final results.

Several PCM fiber counting methods have been published by national [35-36] and international organizations [37-38]. Most countries have methods very similar to the ones referenced here.

e. Sampling volume for asbestos abatement applications

Sampling for asbestos after abatement requires the selection of a sampling volume so that one can have high confidence that the air meets acceptable concentration standards. The following is an example of how to calculate this sampling volume.

The approach assumes that one wishes to select sampling parameters in order to have a high degree of confidence that a target exposure standard (e.g. NIOSH REL, OSHA PEL, EPA clearance standard) is met.

Several factors need to be established in order to perform this calculation if the target exposure standard involves clearance monitoring. The U.S. Environmental Protection Agency (EPA) authorizes the use of PCM for some clearance monitoring applications and specifies that a level of 0.01 fibers/mL be met. On the method synopsis page, Method 7400 indicates that the limit of detection (LOD) for PCM analysis is 5.5 fibers/100 fields. This is based on intralaboratory variability. A major difference between Method 7400 and other analytical methods in the NIOSH Manual of Analytical Methods (NMAM) is that there is no

reference method for Method 7400. Therefore, the consensus mean is the "true" value and the interlaboratory results effectively define the method accuracy. Under the heading "Evaluation of Method, B. Interlaboratory comparability," Method 7400 provides a means of calculating the confidence limits on a single analysis result (Equations 3 and 4). From Equation 3, the interlaboratory variability at the LOD is such that the upper 95% confidence limit on a measured value is 300% greater than (or 4 times) the measured value.

Using the upper confidence limit, the equation in Section 21 in Method 7400 can be used to estimate the sampling volume.

$$\frac{\dfrac{\text{number of fibers}}{\text{area of 100 fields}} \times \text{total filter area}}{\text{sampling volume}} = \frac{\text{target level}}{4}$$

With the appropriate values inserted, the equation becomes

$$\frac{\dfrac{5.5\,\text{fibers}}{0.785\ \text{mm}^2} \times 385\ \text{mm}^2}{\text{sampling volume}} = \frac{0.01\ \text{fiber/mL}}{4}$$

Solving this equation for sampling volume gives 1080 L. This is the minimum volume that will give a result allowing a single sample to indicate compliance with the 0.01 fiber/mL limit with 95% confidence. It requires that the sample give a result less than or equal to the LOD or 5.5 fibers per 100 fields. A higher fiber count may still indicate that the concentration meets the target level, but not with the same level of confidence. This is likely to be a conservative estimate of concentration and additionally ensure compliance with the standard because the fiber concentration is low and, as indicated above, low fiber loadings are usually overestimated. However, the background concentration of non-fibrous dust on the filter also must be low to ensure that fibers are not obscured.

f. Other techniques

Since fiber counting by human analysts produces relatively high biases and variability, several researchers have attempted to develop automated counting systems. With the increases in computer power over the last 25 years, it has been tempting to assume that fiber counting is a solvable problem and significant efforts have been made to develop such a system. The most intensive effort to produce a fiber counting system was carried out by Manchester University in collaboration with the Health and Safety Executive in the UK [39]. The Manchester Asbestos Program (MAP) was able to give reasonably good agreement with human counters for certain types of samples. It was used as a reference analyst for the US and UK reference sample programs for several years. Eventually, the MAP was dropped as the reference because it was not sufficiently consistent for all types of samples.

The principle problems with image analysis of asbestos fibers include: the complexity of many fiber shapes, including bundles, agglomerates, and split fibers; the fibers often go in and out of the plane of focus; the background includes many particles and other non-fibrous shapes; the phase contrast optics produces haloes around particles in the sample that can be detected as fibers; and finally, and perhaps most importantly, the contrast between the fibers and background is poor and many fibers are near the detection threshold. An evaluation of the MAP program indicated that a significant fraction of the fibers were misidentified as multiple fibers, not detected at all, and groups of compact particles or edges of large particles were detected as fibers [40].

Inoue and coworkers have more recently developed image analysis software using a microprocessor-based PC [41]. Initial tests indicate that it works approximately as well as human counters. Inoue also evaluated how well human counters and the image analyzer did in detecting the same fibers in a sample and found that only about 50% of the fibers were consistently counted by all counters, so the image analysis system did approximately as well as the human counters [42]. Further testing of the image analysis system is needed.

In addition to image analysis, optical microscopy can be enhanced using a personal computer to more easily observe the image and to mark and measure fiber dimensions, with automatic recording of the fibers counted [43]. This does not appear to improve the counting accuracy since the analyst still decides which fibers are to be counted.

4. POLARIZING LIGHT MICROSCOPY (PLM) OF BULK MATERIALS
(Adapted from Baron [44])

The asbestos fibers in bulk material can be released and become airborne when the bulk material is disturbed. For this reason, it is desirable to measure the asbestos content of bulk samples. PLM is often used to determine the percent asbestos in bulk material. The EPA [45] has defined asbestos containing material (ACM) as material containing more than 1% asbestos using the PLM method, which effectively estimates concentration by area observed. Some confusion exists regarding the units of asbestos percentage. EPA originally indicated that the limit for ACM was 1% by mass [45], but because of the difficulties in determining corrections for differences in material density and in determining particle volumes, the limit was changed to 1% by area as determined by the PLM method [46]. OSHA does not specify units for percent asbestos in its regulations [47].

Several PLM techniques are used for identifying fiber type as well as semi-quantifying the percent fibrous material (usually asbestos) in a sample [48-52]. These techniques depend on particle shape, the refractive index, and other optical properties of individual particles. Many of these PLM techniques require visual observation of color in the fiber and become less reliable for fibers thinner than about 1 μm [53].

a. Sampling

Several procedures have been suggested for obtaining representative bulk samples of ACM in a fashion that prevents unnecessary exposure to asbestos aerosol [54-56]. Representative sampling of commercial ACM materials is often problematic; these materials may vary significantly in asbestos concentration between nearby locations and even at different depths

at the same location. Sampling from multiple locations and compositing samples helps improve the likelihood of obtaining a representative sample.

The material should be wetted or sealed during sample removal. A small coring device, such as a cork borer, can be used to obtain a sample from the full depth of the material. At least three samples per 1000 ft^2 of ACM should be taken [45]. The sample should be placed in a well sealed, rugged container. Finally, the sampled area should be repaired or sealed to minimize further fiber release.

Surface sampling has been proposed by several groups, but there is no relationship between airborne fibers and those found on surfaces [57]. Therefore, surface sampling for fibers is not recommended.

b. Sample preparation and analysis

Sample preparation for a PLM analysis involves grinding the material to the optimum particle size range (1-15-μm diameter) and dispersing the particles in a liquid of known refractive index on a glass slide [51]. Particle size uniformity in the prepared sample is extremely important. A few large chunks of material may contain more asbestos than hundreds of much smaller particles. Friable material, i.e., that which is crumbly or can be crushed by hand, may readily release fibers and is considered more hazardous. Friable materials are generally easier to prepare for analysis than some other ACMs, such as vinyl asbestos floor tiles, which may require dissolution or ashing of the matrix material so that the fibers are separated and visible in the microscope. Before and after preparation, the sample is observed with a stereomicroscope at 10-100X magnification to evaluate sample uniformity and observe whether fibrous material is present.

Some materials that interfere with accurate fiber identification either by their similarity or by covering up the fibers can be removed by physical treatment of the sample. For instance, organic materials, such as cellulose fibers or diesel soot can be removed by low temperature, oxygen-plasma ashing [58]. Leather fibers and chrysotile have a similar appearance and refractive index. The leather can be removed by ashing at 400°C [59].

Fiber morphology, i.e. the structure and shape of the fiber, can be used to assist in its identification. Morphology of fibers can give some indication of fiber type. For instance, chrysotile fibers tend to be curly, while amphibole fibers are straight, especially when they are shorter than 50 μm. Asbestos fibers often have frayed or split ends, while glass or mineral wool fibers are typically straight or slightly curved with fractured or bulbous ends. Many plant fibers are flattened and twisted, with diameters between 5-20 μm. Note that it is not recommended to base identification solely on morphology.

Fiber refractive index and other crystalline properties can be used to identify fiber type with reasonable certainty. Several techniques for determining these properties can be used in a polarizing light microscope. When viewed in the microscope with crossed polarizing filters, isotropic (isometric or amorphous) fibers appear consistently bright when rotated, while anisotropic (uni- or biaxial crystal structure) fibers appear bright, but disappear when rotated to their extinction angle, which is a function of crystal structure. Thus, amorphous materials such as glass or mineral wool fibers can easily be discriminated from asbestos.

During PLM analysis, fibers are immersed in a fluid selected to have a known refractive index. When a fiber has a larger refractive index than the surrounding fluid medium, the bright halo (Becke line) around that fiber appears to move into it as the microscope focus is raised; when the fiber has a smaller refractive index, the Becke line move out of it. Placing the fibrous material into several different refractive index fluids allows the fiber refractive index to be bracketed.

Dispersion, or refractive index change with wavelength, of a fiber can be used for identification. When particles are placed in a liquid whose dispersion is different from that of the particle, the particle may exhibit a color caused by the refraction of light. This technique requires the use of special "dispersion staining" optics. By using several refractive index liquids in series, the refractive index and the dispersion of the fiber can be established and compared with those of standard materials or published data [12].

Once the sample has been uniformly dispersed on a slide in the appropriate refractive index liquid, specific fiber types, e.g., asbestos, can be identified and the percent fibers estimated. Two approaches are typically used: visual comparison with prepared reference slides or pictures and point counting. When attempting to estimate whether a material is ACM (i.e., > 1% asbestos), the visual comparison technique is adequate when more than about 10% of the particles observed are asbestos. Point counting is used for lower concentration samples to provide higher accuracy [60]. It involves observing 400 or more randomly selected "points" (identified with a reticle crosshair) in the sample. The number of points containing asbestos is divided by the total number of points observed to give the percent asbestos. A combination of these approaches balances the analysis time and accuracy of the results [61].

PLM also can be used for qualitative analysis of air sample filters by collapsing the filter and using low temperature plasma etching of the surface to expose the fibers. Various refractive index liquids can then be placed on the etched surface to surround the fibers, allowing techniques noted above to be used [53]. The smallest fibers that can be identified by this method are about 1-μm diameter.

c. Accuracy

PLM analysis is primarily used for qualitative identification of fiber type. Accurate identification of asbestos and other fibers requires proper training in the crystallographic properties of particles as well as training and familiarization with the PLM. As with fiber counting, a laboratory quality assurance program is necessary to ensure consistently accurate results. The National Voluntary Laboratory Accreditation Program (NVLAP) operated by the National Institute for Standards and Technology (NIST) inspects laboratories for proper practice as well as providing unknown samples four times a year to check their performance in fiber identification. Under a predecessor to this program, approximately 350 laboratories correctly classified 98.5% of the samples as asbestos and correctly identified the specific asbestos types in approximately 97% of the samples. A blind test of 51 laboratories resulted in 97.5% correct classifications and 79.1% correct identifications [62]. The American Industrial Hygiene Association Proficiency Analytical Testing Program provides similar PLM audit samples to laboratories. Some common interferences for bulk analysis by PLM include sepiolite, vermiculite, and cleavage fragments of non-asbestos amphiboles.

PLM has been cast in a quantitative measurement role by the EPA requirement of determining whether a school building material meets the 1% asbestos level defining ACM. Many variables including particle size, density and shape are not adequately controlled or measured in the analysis and contribute to errors in the percent mass estimate. Thus, PLM analysis is at best a semi-quantitative technique.

Chatfield indicated that the accuracy of PLM for low concentrations of asbestos was poor and described a set of procedures that concentrated the asbestos into a weighable fraction [63]. An EPA report describes, in addition to the PLM and Chatfield's gravimetry methods, a TEM and an X-ray diffraction method for bulk analysis of asbestos [63]. NIOSH Method 9000 describes an X-ray diffraction method for chrysotile.

5.   ELECTRON MICROSCOPY

Scanning electron microscopy (SEM) has not been the focus of as much method development as either light microscopy or transmission electron microscopy (TEM). PCM found favor because of the low equipment cost and lower training level required for analysis. TEM is preferred for environmental and research studies because it offers the highest resolution and the most positive identification capabilities. TEM allows visibility of all asbestos fibers down to the individual fibrils, electron diffraction for crystal structure identification, and energy dispersive x-ray analysis for elemental measurement.   SEM has intermediate resolution, with many instruments of this type not able to see all asbestos fibers. However, many modern SEMs have the capability of detecting asbestos fibrils, though contrast with background may be poor for some fiber types, especially if a high contrast substrate is not used.   Energy dispersive x-ray analysis is also available for many SEMs, providing some qualitative information of fiber type. However, since electron diffraction typically cannot be performed by SEM, this often leaves open the question of positive identification of fibers.

6.   SCANNING ELECTRON MICROSCOPY (SEM)

Particles are observed in the SEM when a beam of electrons is focused onto the sample surface and scanned over an area.   The electrons are scattered from the surface and detected above the surface synchronously with the beam scan rate and an image of the scanned surface is created. Thus, the SEM measures the surface of particles on a substrate. The best image can be obtained on conducting objects deposited on a smooth, conducting substrate. Particles are often deposited on aluminum or carbon planchets that fit directly into the SEM or onto polycarbonate membrane (track-etched, Nuclepore®) filters. The samples are usually coated with gold or carbon to increase conductivity.

There have been some SEM methods developed for fiber counting [65-68]. These methods are primarily used for inorganic man-made fibers that have larger diameter fibers than can occur with asbestos. Thus, all the fibers are potentially visible using the SEM.

7.   TRANSMISSION ELECTRON MICROSCOPY (TEM)

The transmission electron microscope (TEM) allows detection of particle shape and structure down to the smallest asbestos fibers (Figure 2) and can be used to determine crystal structure from electron diffraction as well as determining elemental composition from energy

dispersive x-ray analysis. Although TEM analysis is potentially very powerful and accurate, the process of sample collection and preparation and details involved in sample analysis can degrade the quantitative accuracy of the technique. Several more specialized techniques, such as electron energy loss spectroscopy and secondary ion mass spectrometry, have been used for analyzing particles and can also be applied to fibers [69].

Airborne fiber samples for TEM analysis are typically collected onto a filter, usually a polycarbonate membrane or MCE membrane filter. For the latter filter type, the filter is chemically collapsed to form a smooth upper surface on which collected fibers are trapped. Sometimes the surface is etched using a low temperature asher to expose the fibers collected on or near the surface of the original filter. The filter is coated with a carbon film that entraps fibers exposed on the filter surface and the filter material is then dissolved away. The carbon film is transferred to a TEM grid (usually 3-mm diameter) and the sample can be placed in the TEM for analysis.

For Method 7402, the surface is not ashed because some fibers, e.g., cellulose, may be removed and give an inaccurate total fiber count [58]. Ashing can thus affect the measurement of the asbestos fiber fraction.

The above approach to preparing MCE filters for TEM analysis is called the direct-transfer approach, since fibers are transferred to the carbon film with minimum disturbance to the way they were collected. An alternative technique is to dissolve the entire filter in liquid, ultrasonicate the suspension to disperse the particles, and deposit an aliquot of the particle suspension onto a polycarbonate filter for final transfer to the carbon film. This is called the indirect transfer technique. With the indirect technique, the optimum particle loading of the TEM sample can be obtained and soluble particles can be removed from the sample. However, the suspension process can change the apparent size distribution of the particles and fibers by breaking apart agglomerates or even breaking apart asbestos fibers into smaller fibers or fibrils [70]. The breakup problem can be especially severe for chrysotile, causing a large increase in fiber count. Quality assurance is especially important with TEM analysis of fibers. The NVLAP program provides quality assurance accreditation for laboratories performing TEM analysis using the Environmental Protection Agency's Asbestos Hazard Emergency Response Act (AHERA) method. Note that data provided under the AHERA method, because of significant differences in counting rules, the types of structures counted as asbestos, and the size range of fibers, cannot be directly compared with counts by Methods 7400 or 7402.

The process of sample collection and preparation is a complex one that can introduce biases into the final measurement. Since only small portions of the filter are measured during TEM analysis, sampled fibers that deposit non-uniformly onto the filter due to inertial, gravitational, and electrostatic effects will be measured inaccurately [71]. Fibers that penetrate the filter surface and are not transferred to the carbon film will be lost. If the filter is incompletely dissolved away from the carbon film, the sample will be difficult to analyze.

Many of the sources of bias and variability noted in sampling and counting by PCM also apply to TEM analysis. Fiber counting in a TEM can also introduce biases and variability in the final result. There is a tendency to use the high magnification of the TEM to look for the smallest fibers, while ignoring some of the larger ones. Even so, fibers shorter than 0.5 µm tend to

be missed because they are difficult to see in the background clutter of the sample [72]. Taylor et al. found that TEM counting gave poorer precision than counting the same sample by PCM and recommended that the fraction of asbestos fibers counted by TEM be applied to the PCM count as indicated in Method 7402 [73]. This combined PCM/TEM approach gave better precision than counting by TEM alone.

In addition to recognizing fibrous shape and structure of the several asbestos minerals, qualitative analysis of fibers by TEM primarily involves two techniques, energy dispersive x-ray analysis and electron diffraction. X-ray analysis produces responses for each of the elements (typically atomic number > 6, but is instrument dependent) present in a particle; the responses occur as peaks in an energy spectrum. Specific asbestos minerals can be identified using peak intensity ratios observed in standard samples and as specified in the method.

The crystal structure of individual fibers is evaluated using electron diffraction. Focusing the TEM electron beam on a single fiber produces a diffraction pattern consisting of a number of spots. The spot locations depend not only on the particle crystal structure, but also on the geometry of the electron beam optics and other instrumental parameters. The diffraction spot locations relative to one another give a very specific identification of crystal structure. For easily recognized minerals, such as chrysotile, the visual identification of the diffraction pattern is often sufficient. However, to identify fibers not fitting the x-ray analysis pattern for standard asbestos minerals, careful measurement, or indexing, of the diffraction spots is important.

The combination of x-ray analysis and electron diffraction gives a highly definitive identification of specific minerals. However, as with any analytical methods, there are exceptions that require greater expertise to recognize potential interferences. Some minerals that are difficult to differentiate from regulated asbestos minerals include non-regulated amphiboles and fibrous talcs. There are several established methods for analyzing fibers, especially asbestos fibers, by TEM [45, 74-77].

8.   OPTICAL DETECTION (LIGHT SCATTERING)

Two types of light scattering detectors are commonly used for measuring airborne dust concentrations: the optical particle counter (OPC), which detects and counts individual particles, and the photometer (sometimes called a nephelometer), which detects the scattering from all particles in a defined detection volume. A standard OPC was used to detect asbestos concentrations in a workplace where the aerosol was primarily fibrous and good correlation with fiber counts was obtained [78]. A nephelometer may also be used, but may have an even greater interference from non-fibrous dusts.

The fibrous aerosol monitor (Model FM-7400, MIE, Inc. Bedford MA) used an electrostatic alignment technique by applying a field that aligns and rotates individual fibers in a laser beam. The light scattered from the fibers uniquely identified the presence of individual fibers. This allowed specific detection of fibers [79] and was even used to measure fiber length [80].

Several field tests have indicated that the fibrous aerosol monitor agrees reasonably well with field measurements of fibers by phase contrast microscopy, though mostly at concentrations above ambient levels. It has been used at abatement sites to provide rapid feedback and ensure acceptable containment of airborne fibers during asbestos removal.

9.   FIBER CLASSIFICATION

Several devices have been used to measure or separate fibers by diameter. A spiral centrifuge was used to separate fibers and reference spherical particles to estimate fiber aerodynamic diameter [81]. It was found that the aerodynamic diameter was directly proportional to physical diameter, proportional to the square root of the fiber density, and proportional to fiber length to the 1/6th power. For mineral fibers having a density of about 3 g/cm^3, the aerodynamic diameter was approximately three to five times the physical diameter of the fiber. Behavior of glass fibers in a cascade impactor was investigated by Burke and Esmen [82]. A small correction to the aerodynamic diameter was developed to take into account interception of longer fibers with the impaction surface. An inertial spectrometer was used to measure fiber aerodynamic diameter and good diameter separation was achieved [83]. Baron and Deye developed a technique for separating fibers by length using dielectrophoresis [84, 85]. This technique was also shown to be useful for measuring fiber length and diameter distributions [86].

As with most airborne dusts, fiber settling will reduce the number of larger diameter fibers in a distribution as the distance from the source of the dust increases. Esmen et al. showed that average fiber concentration in workplaces decreased exponentially with an increase of fiber diameter, indicating that the larger diameter fibers settled out more quickly than smaller diameter fibers [87]. Cyclones, impactors and porous foam classifiers were evaluated for efficiency of removing airborne fibers not likely to deposit in the lungs [88].

The aerodynamic diameter of fibers is dependent primarily on fiber physical diameter and fiber density, with a minor dependence on fiber length [89]. The diseases caused by asbestos fibers are lung diseases and so it makes sense to measure only fibers that can enter the lungs, i.e., thoracic fibers. Identical conventions for thoracic samplers have been published by ISO, ACGIH [90], and CEN. Baron [89] showed that sampling fibers with a thoracic sampler was approximately equivalent to counting only mineral fibers with a physical diameter smaller than 3 µm. Jones et al. [91] reported that there appeared to be no impediment to using a thoracic sampler for fiber sampling; they found that several samplers matched the thoracic convention, the sample collected by these samplers could be analyzed by standard methods, and that field studies indicated equivalence to the current method. Maynard [92] also found that there appeared to be no variation in penetration through these samplers as a function of fiber length. The advantage to using a thoracic sampler, apart from adhering to conventional sampling practice, is that it would remove larger compact particles and fibers from the sample and result in a cleaner sample. Although current US practice does not use an upper diameter limit for asbestos fibers, such a limit is commonly used for man made fibers. Except for the United States, all national and international organization methods use an upper diameter limit of 3 µm for fiber counting of asbestos fibers.

It is likely that thoracic sampling will eventually be in routine use for measurement of asbestos and other fibers. This approach has several advantages. It places the fiber method in line with other dust sampling conventions. It removes some of the larger particles in the sample, resulting in a cleaner sample for the analyst. It removes the need for determining fiber diameter during counting and it is consistent with previous practice of using an upper diameter limit of 3 µm for fiber counting in some methods. Thoracic sampling has the disadvantage of requiring the flow rate for a specific sampler to be fixed. This reduces the flexibility to target the loading of the filter by adjusting the flow rate. However, several classifiers can be designed to operate at selected flow rates to allow some flexibility in sampling.

10. CONCLUSIONS

The capability for measurement of fiber size distributions is available through microscopy and, to a much lesser extent, through direct-reading instrumentation. Because of differences in counting rules, resolution capability, and ability to distinguish asbestos from interfering particles or other fibers, PCM, PLM, SEM, and TEM methods often do not produce results which are directly comparable. The traditional methods of microscopy are relatively inaccurate when compared to chemical analysis methods for most other analytes because of the many sources of error in the sampling and analysis procedure. To improve laboratory-to-laboratory agreement, counter training and quality control, including the exchange of samples among laboratories and proficiency testing, are important. Implementation of training through the use of Pang's coverslips allows investigation of counting errors and potential improvement of PCM counting accuracy. Thoracic sampling could eliminate interfering particles and thereby improve measurement methods in the future.
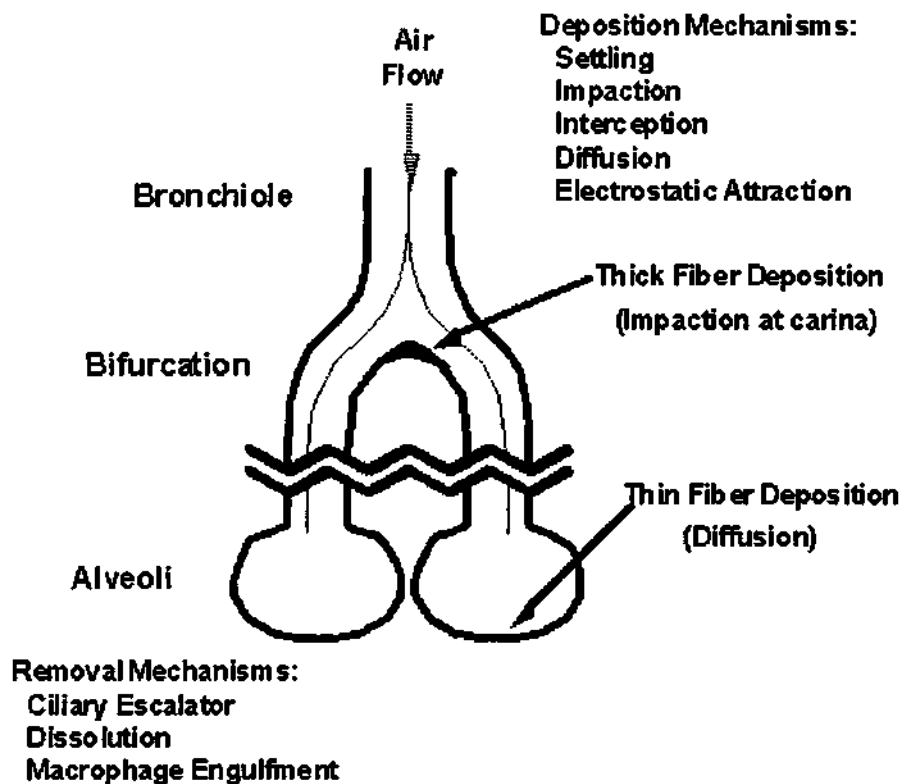
Figure 1. Schematic of mechanisms that affect fiber deposition and retention in the lungs. The deposition depends on all the indicated parameters in a complex fashion. However, larger diameter particles are affected more by gravitational settling, impaction, and interception, resulting in greater deposition further up in the respiratory tract. The saddle points, or carinae, in the branching respiratory tree are often a focal point for deposition of larger diameter fibers. Smaller diameter particles are affected more by diffusion and can collect in the smaller airways and gas exchange region (alveoli). Particle removal from the lungs is primarily effected by the cilia coating the non-gas exchange regions of the lungs; the cilia push mucus produced in the lungs and any particles trapped in the mucus out of the lung and into the gastrointestinal tract in a matter of hours or days. Some fibers are sufficiently soluble in lung fluid that they can disappear in a matter of months. Finally, white blood cells or macrophages roam the gas exchange regions and ingest particles deposited there for removal through the lymph system. Human macrophages are approximately 17 μm in diameter and can only ingest particles smaller than they are. Therefore, thin fibers are likely to deposit in the gas exchange region and, of these, the long insoluble fibers can remain in the lungs indefinitely.

Fiber Health Indices* and Measurement Methods

Length (μm) Diameter	< 0.5	0.5 - 2	2 - 5	5 - 10	10 - 50	>50
< 0.1 μm						
> 0.1 - 0.25 μm						
> 0.25 - 1.0 μm						
>1.0 - 3.0 μm						
> 3.0 μm						

\\\\\\ Mesothelioma

////// Lung cancer
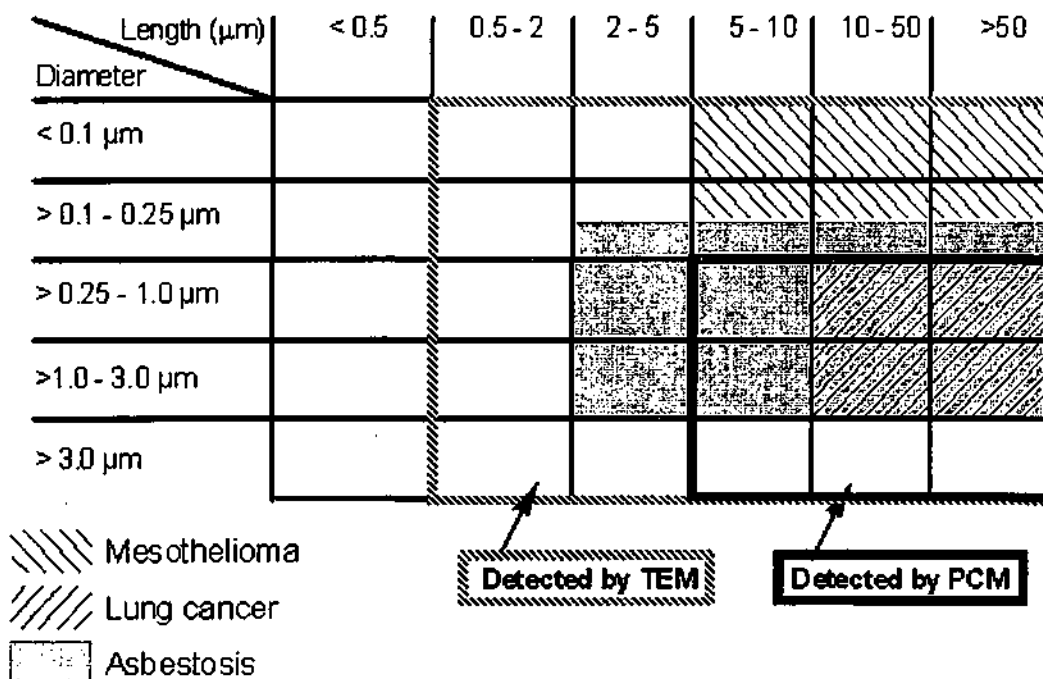
Asbestosis

*Indices proposed by Lippmann[2]

Detected by TEM

Detected by PCM

* Lung cancer and mesothelioma are more likely to occur at current occupational and environmental levels than asbestosis

* PCM can cover only a portion of the total fiber distribution; PCM is used as an indicator of total exposure

* TEM can cover the entire size range, but most methods emphasize one size range over another through selection of magnification and counting rules

Figure 2. Comparison of proposed size ranges of asbestos fibers causing specific diseases compared with the fiber sizes detected using TEM and PCM techniques.

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CATION SITE ASSIGNMENT, CLASSIFICATION, AND OPTICAL PROPERTIES OF ELEVEN LARSEN AMPHIBOLES

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The classic studies of alkali rocks of Iron Hill, Colorado by E. S. Larsen (1941) contain a wealth of chemical composition and optical properties of rock-forming minerals, including 11 amphiboles mostly from Iron Hill and other localities as shown in Table 1 (Table 20 in Larsen 1941) below.

Table 1. Analysis and optical properties of amphiboles from Iron Hill, Colo., Libby, Mont., and Trinity County, Calif.

The lack of X-ray diffraction data as well as the rather limited understanding of the extremely complicated crystal chemistry of amphibole family in 1940's made it impossible to classify these amphiboles into proper amphibole mineral names. Instead of assigning mineral names based than the acceptable nomenclature at that time, Larsen calculated the percentages of end-members, such as tremolite, soda-tremolite, actinolite, soda-actinolite, glaucophane, hastingsite, etc., based on the chemistry. The end member percentages, however, can not readily be translated into the amphibole names in accordance with IMA (International Mineralogical Association) nomenclature of amphiboles (Leake et al., 1997 and 2004).

Using the IMA site assignment guidelines illustrated in Fig. 1(Larsen, 1997; Schumacher, 1991) and amphibole nomenclature (Leake, 1997 and 2004), I classified the 11 Larsen amphiboles based the original chemical analysis and stoichiometric limitations into *6 richterite, 2 magnisioarfvedsonites, and 4 magnisiohastingsites* based on their cation site assignment results detailed in Table 2.
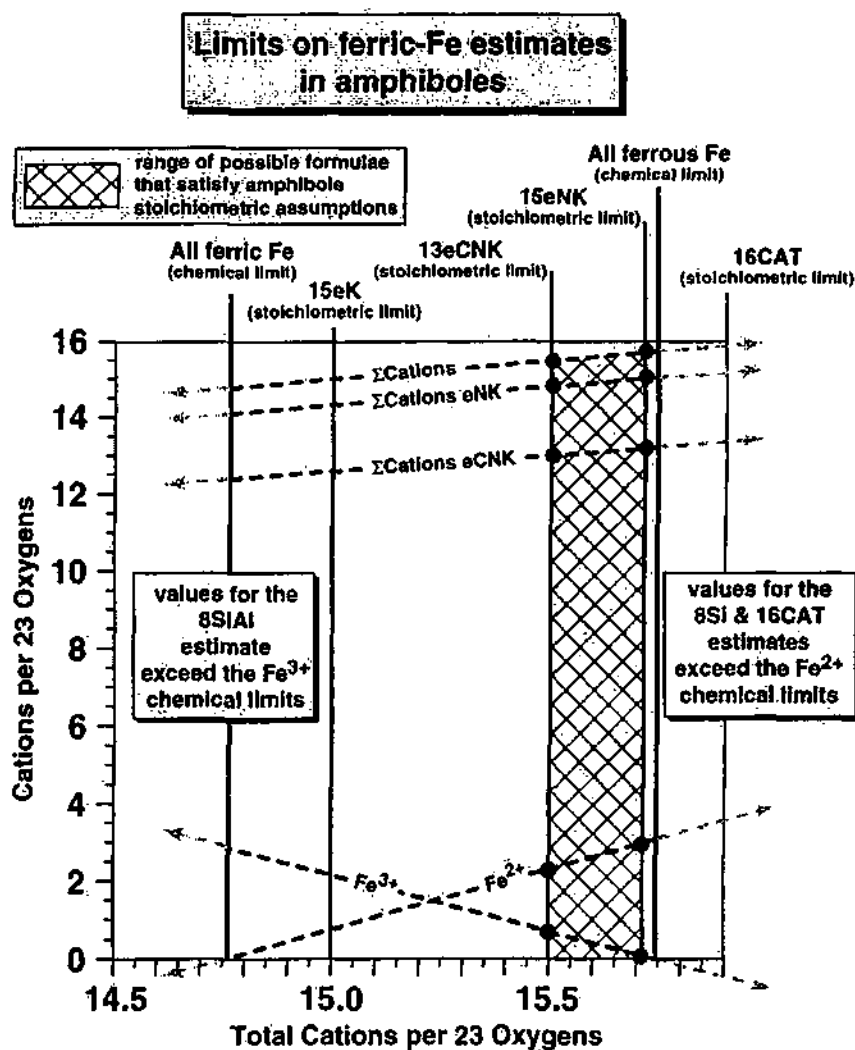
Figure 1. Summary of ideal site-assignments, limits of various cation subtotals, and the type of correction (minimum or maximum) that can be obtained by calculating the formulae to these stoichiometric limits (Leake et al., 2003).

Table 2. Chemical composition and optical properties of amphiboles from Iron Hill, Colorado, Libby, Montana, and Trinity County, California*

Amphibole Group** Mineral Name Locality	3 (sodic-calcic amphiboles) Richterite California	Montana	Colorado	Colorado	4 (sodic amphiboles) Magnesioarfvedsonite Colorado		3 (sodic-calcic amphiboles) Richterite Colorado		2 (calcic amphiboles) Magnesiohastingsite Colorado			
Sample ID	a	1	2	3	4	b	5	6	7	8	9	10
Si	7.92	7.95	7.84	7.63	7.60	8.03	7.53	7.50	6.36	6.01	5.96	5.74
Al	0.33	0.12	0.05	0.71	0.33	0.20	0.54	0.66	1.85	2.01	2.49	2.67
Ti	0.00	0.03	0.02	0.06	0.01	0.03	0.27	0.06	0.10	0.08	0.20	0.36
Fe3+	0.00	0.49	0.41	0.47	0.78	0.90	1.06	0.75	0.44	0.71	0.52	0.57
Mg	4.35	4.61	4.28	3.91	3.73	3.70	3.21	3.36	3.50	3.58	3.28	2.25
Fe2+.Mn2+	0.61	0.21	0.35	0.69	0.41	0.31	0.50	0.83	0.90	0.31	0.74	1.53
Ca	0.75	0.93	0.76	1.00	0.50	0.40	0.61	0.69	1.53	2.06	2.03	2.00
Na	1.96	1.36	1.46	1.60	2.11	2.24	1.94	2.03	1.30	0.94	0.62	1.06
K	0.00	0.32	0.54	0.40	0.38	0.32	0.08	0.15	0.12	0.13	0.36	0.00
T***												
Si	7.92	7.95	7.84	7.63	7.60	8.03	7.53	7.50	6.36	6.01	5.96	5.74
Al	0.08	0.05	0.05	0.37	0.33	0.00	0.47	0.50	1.64	1.99	2.04	2.26
Ti	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sum	8.00	8.00	7.91	8.00	7.94	8.03	8.00	8.00	8.00	8.00	8.00	8.00
C***												
Al	0.47	0.07	0.00	0.34	0.00	0.20	0.07	0.16	0.21	0.02	0.45	0.41
Ti	0.00	0.03	0.00	0.06	0.00	0.03	0.27	0.06	0.06	0.08	0.20	0.36
Fe3+	0.00	0.49	0.41	0.47	0.78	0.90	1.06	0.75	0.44	0.71	0.52	0.57
Mg	4.35	4.41	4.28	3.91	3.73	3.70	3.21	3.36	3.50	3.58	3.28	2.25
Fe2+.Mn2+	0.18	0.00	0.31	0.22	0.41	0.17	0.39	0.67	0.79	0.31	0.55	1.41
Sum	5.00	5.00	5.00	5.00	4.92	5.00	5.00	5.00	5.00	4.70	5.00	5.00
B***												
Mg	0.00	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe2+.Mn2+	0.43	0.21	0.04	0.47	0.00	0.14	0.11	0.16	0.11	0.00	0.19	0.12
Ca	0.75	0.93	0.76	1.00	0.50	0.40	0.61	0.69	1.53	2.06	2.03	2.00
Na	0.82	0.66	1.20	0.53	1.50	1.70	1.28	1.15	0.36	0.00	0.00	0.00
Sum	2.00	2.00	2.00	2.00	2.00	2.24	2.00	2.00	2.00	2.06	2.22	2.12
A***												
Na	1.14	0.70	0.26	1.07	0.61	0.54	0.66	0.88	0.94	0.94	0.62	1.06
K	0.00	0.32	0.54	0.40	0.38	0.32	0.08	0.15	0.12	0.13	0.36	0.00
Sum	1.14	1.02	0.80	1.47	0.99	0.86	0.74	1.03	1.06	1.07	0.98	1.06
α	1.606	1.612	1.606	1.628	1.623	—	1.651	1.650	1.653	1.653	1.665	1.680
β	1.613	1.623	1.616	1.638	1.633	1.63	1.661	1.657	1.663	1.661	1.674	1.693
γ	1.623	1.627	1.623	1.644	1.641	—	1.670	1.659	1.670	1.669	1.685	1.702
$\Delta(\gamma-\alpha)$	0.017	0.015	0.017	0.016	0.018	—	0.019	0.009	0.017	0.016	0.020	0.022
2V(°)	—	Lge	Med. Lge	82	87	—	72	64±	64	90	90	Lge
Dispersion	—	Not perc.	Not perc.	p>v	p>v sig.	—	p>v sig.	—	Slight	p>v sl.	p>v sl.	p>v sl.
γ_{roster}^c(°)	—	20.5	24	—	—	—	56.5	—	39	28	—	22
γ_{Dqslow}^c(°)	0±	20.5	24	24	Av. 40±	51	57.0	34.8	40	27.5	26.5	21.5
γ_{fast}^c(°)	—	20.5	24	—	—	—	57.5	36.0	40.5	28	26.5	21
Pleochroism α	Colorless	Olive green	Colorless	Nearly colorless	Nearly colorless	—	Pale apple green	Pale yellow	Pale yellow	Very pale green	Pale brown	Pale yellowish brown
β	Colorless	Pale yellow	Colorless	Pale greenish brown	Smoky blue	—	Pale green	Dark olive green	Dark green	Pale green	Brownish green	Brown
γ	Pale yellow green	Pale pure green	Colorless	Light green	Blue-green	—	Dark violet-brown	Pale green	Light green	Light blue-green	Blue-green	Very dark brown
Specific Gravity	—	3.051	3.066	3.14	3.129	—	3.132	3.137	3.16	3.14	3.189	3.27

* Larsen, E. S., (1941)
** Leake, B. E. et al. (2004)
*** Leake, B. E. et al. (1997)

The amphibole that is of special interest to Libby project is richterite. Although 6 of Larsen amphiboles are classified as richterite based on $(Na+K)_A \geq 0.50$, $(Ca+Na_B) \geq 1.00$, and $0.50 < Na_B < 1.50$, Nos. 5 and 6 (Table 2) exhibited significantly anomalous optical properties such as high refractive indices, high extinction angles (to the extent that No. 5's elongation sign becomes negative as its $\gamma \wedge c$ exceeds 45°), and strong $p > v$ dispersion, which might have been

caused by significantly higher $(Fe^{3+}+Fe^{+2}+Mn^{2+})$ content ranging from 1.56 to 1.58 as compared with the range of 0.61 to 1.16 of the other 4 richterites.

Therefore, only the first 4 richterites (a, 1, 2, and 3, Table 2) are used to expand the Libby Amphibole Table (Su, 2005). Table 4 is a summary of Larsen amphiboles excluding the two richterites with high total iron content.

Table 3. Summary of optical properties of 6 richterites, 1 magnesioarfvedsonite and 4 magnesiohastingsite (Larsen, 1941)

Amphibole	α	γ	Δ	$\gamma \wedge c(°)$	Pleochroism
Richterite (normal Fe)	1.606-1.628	1.623-1.644	0.015-0.017	20.5-24	Colorless to Olive green
Richterite (high Fe)	1.650-1.651	1.659-1.670	0.009-0.019	34.8-57	Pale green to violet brown
Magnesioarfvedsonite	1.623	1.641	0.018	40±	Colorless to blue green
Magnesiohastingsite	1.653-1.680	1.670-1.702	0.017-0.022	21.5-40	Pale yellow to dark brown

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A rapid and accurate procedure for the determination of refractive indices of regulated asbestos minerals

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ABSTRACT

By using dispersion staining methods and pre-constructed conversion tables, it is possible to quickly and accurately determine two principal refractive indices (RI) of the six regulated asbestos minerals, chrysotile, grunerite (amosite), riebeckite (crocidolite), tremolite, actinolite, and anthophyllite, in a single immersion oil mount. This procedure is especially suitable for commercial environmental laboratories specializing in the analysis of asbestos components in bulk building materials. The effectiveness of this practical procedure has been proven through rigorous testing and extensive usage over the last decade by the majority of environmental laboratories in the U.S. The principle of this procedure is also readily applicable to RI determination in other applications: mineralogy, forensics, pharmaceutical research, particle identification, etc.

INTRODUCTION

Upon the enactment of the Asbestos Hazard Emergency Response Act (AHERA) in 1986, the U.S. Environmental Protection Agency (EPA) authorized the National Institute of Standards and Technology (NIST) to add bulk asbestos and airborne asbestos analyses to the National Voluntary Laboratory Accreditation Program (NVLAP) for the purpose of monitoring the quality performances of hundreds of American environmental laboratories specializing in asbestos analysis. NVLAP accreditation is required for any commercial laboratories engaging in work related to asbestos survey, abatement, and monitoring projects at American public schools. To meet the requirements set forth by EPA (1993) and NIST (1994), analysts must measure and record two principal refractive indices, n_α and n_γ, of every type of asbestos mineral found in bulk samples. Facing a daily workload of 60 or more samples, analysts must be able to quickly determine the RI of suspected asbestos minerals with an accuracy ±0.005 to 0.010 as required by the NVLAP. The Becke line method is too time-consuming because more than one preparation is needed to bracket the RI of every type of asbestos minerals in a sample. Therefore, the dispersion staining method (McCrone 1987; Su 1998) became the method of choice because of its simplicity and effectiveness. Tens of thousands of bulk asbestos samples are being analyzed every day; the significance of any procedure that facilitates this special environmental analysis cannot be overemphasized.

DISPERSION STAINING

The dispersion staining (DS) method uses a central stop (CS) or an annular stop (AS) at the back focal plane of a 10× objective lens to block (CS mode) or single out (AS mode) the wavelength at which the RI of a solid particle equals that of the surrounding immersion liquid (Su 1998). This wavelength is

defined as the matching wavelength, λ_0 (McCrone 1987) or λ_m (Bloss 1999), at which the dispersion curve of the solid intersects that of the liquid. The DS color forming at the edge of the solid particle is a function of λ_0 and the dispersion property of both the solid and the liquid. In the CS mode, it consists of a mixture of wavelengths in the visible spectrum with λ_0 removed by the central stop. In the AS mode, it consists of λ_0 with the rest of the visible spectrum removed by the annular stop. It has been proven (Su 1993) that n_D^S, the RI of the solid at λ_D, Fraunhöfer spectral D line (589 nm), is related to λ_0 and the dispersion coefficients of the solid and the liquid by the following equation:

$$n_D^S = n_D^L + (\Delta^L - \Delta^S)\, k_D \tag{1}$$

where n_D^L = the refractive index of the liquid at λ_D and the temperature of the liquid T in °C;

Δ^L = the dispersion coefficient, $(n_F - n_C)$, of the liquid, where n_F is the RI at λ_F, Fraunhöfer spectral F line (456 nm), and n_C is the RI at λ_C, Fraunhöfer spectral C line (656 nm);

Δ^S = the dispersion coefficient, $(n_F - n_C)$, of the solid;

k_D = a coefficient related to λ_0 and Fraunhöfer F, D, and C wavelengths in accordance with Hartmann dispersion relationship (Bloss 1981), which is equal to

$$[(\lambda_0 - 200)^{-1} - (\lambda_D - 200)^{-1}]/[(\lambda_F - 200)^{-1} - (\lambda_C - 200)^{-1}] \text{ or}$$
$$[(\lambda_0 - 200)^{-1} - 0.002571]/0.001304.$$

It should be emphasized that Equation 1 is based on the dispersion coefficients of both the immersion oils and asbestos minerals. Almost every environmental laboratory in the U.S. uses immersion oils manufactured by Cargille Laboratories. Because the manufacturer has adopted fixed formulations for its products, the dispersion coefficients for the oils used in asbestos identification (Series E for 1.500 to 1.640 and Series B for 1.642 to 1.700) remain unchanged over the years.

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Table 1 lists typical RI values of the six regulated asbestos minerals. Although the absolute RI values of the same type of asbestos minerals from different localities and environments may vary in a significant range, their dispersion coefficients $(n_F - n_C)$ generally remain constant within experimental errors. This is because any factor that increases (or decreases) n_D will also increase (or decrease) n_F and n_C at the same time, resulting in an unchanged $(n_F - n_C)$ or an $(n_F - n_C)$ with negligible change. For an asbestos mineral immersed in an immersion oil, both n_D^L and Δ^L are known for the oil and Δ^S is known for the asbestos; n_D^S is then directly related to k_D or λ_0.

THE OPERATION PROCEDURE

Preliminary identification of suspected fibrous components by stereo microscopy

Preliminary identification of suspected asbestos components is done by studying the material under stereomicroscope. Grayish to whitish curly fiber bundles are usually chrysotile, which comprises more than 95% of asbestos found in building materials. Straight fibers are usually amphiboles, among which only amosite and crocidolite are commonly present in building materials. Crocidolite has a dark blue color whereas amosite is generally gray to light brown. Tremolite, actinolite, and anthophyllite are rarely seen in building materials. In most cases, experienced analysts can reach a fairly accurate preliminary identification of the fibrous components that are suspected to be asbestos minerals through stereomicroscope examination.

Preparation of immersion oil mounts

The suspected asbestos fiber should be mounted in the oil specified in Table 1. If more than one type of asbestos is found and different oils are needed, prepare separate mounts using the corresponding oils. In the RI range of 1.500 to 1.640, Cargille offers two series of oils: Series A (normal dispersion) and Series E (high dispersion). For dispersion staining applications, Series E is exclusively used in asbestos identification because the greater the $(\Delta^L - \Delta^S)$ value, the more distinctive the CSDS color. The procedure described in this paper is based on Series E oil for oils between 1.500 and 1.640. For oils above 1.640, Series B is used because it is the only series manufactured by Cargille Laboratories.

Confirmation of the preliminary identification of asbestos species by polarized light microscopy (PLM)

The six asbestos minerals can be easily identified under a polarized light microscope by examining their color, pleochroism, dispersion staining colors, birefringence, extinction behaviors, and elongation sign (McCrone 1987). The current regulations do not require the differentiation of tremolite from

actinolite by PLM. They can be reported to be tremolite, actinolite or tremolite/actinolite.

Observation of the CSDS (central stop dispersion staining) colors of asbestos fibers

The CS mode is preferred in asbestos RI determination because it produces vivid DS colors against a dark background. By aligning a confirmed asbestos fiber's n_α, which is perpendicular to fiber elongation axis for chrysotile and amosite or parallel to fiber elongation axis for crocidolite, or n_γ, which is parallel to fiber elongation axis for chrysotile and amosite or perpendicular to fiber elongation axis for crocidolite, parallel to the vibration direction of polarizer, the respective CSDS colors can be easily observed.

Because it is impossible to obtain interference figures on fine fibrous tremolite, actinolite, and anthophyllite, statistical observation is used to estimate n_α and n_γ. To estimate n_α, analysts randomly select a fiber, rotate it to the extinction position when the fiber elongation axis is nearly parallel (tremolite or actinolite) or exactly parallel (anthophyllite) to the N-S cross hair (assuming the vibration direction of polarizer is E-W) and observe its CSDS color. After 10 to 20 fibers are examined in this way, the fiber with the longest λ_0 is assumed to exhibit the RI value closest to n_α. To estimate n_γ, 10 to 20 fibers are examined at the extinction position when the fiber elongation axis is nearly parallel (tremolite or actinolite) or exactly parallel (anthophyllite) to the E-W cross hair; the fiber with the shortest λ_0 is then assumed to exhibit the RI value closest to n_γ.

Conversion of an observed CSDS color to the corresponding matching wavelength λ_0

By referring to Table 2 (McCrone 1987), the observed CSDS color can be quickly converted into the corresponding λ_0 by direct match or interpolation based on the hue, saturation, and intensity of the observed CSDS color. As in the case of Becke line method, with proper training and sufficient practice, an analyst's ability to estimate λ_0 from CSDS colors can ensure the 0.005 to 0.010 accuracy required by the regulatory agencies. To further improve the accuracy of λ_0 estimation, analysts should calibrate the particular polarized light microscope used in routine analysis by examining standard reference materials whose n_α and n_γ are accurately known.

TABLE 1. Refractive indices and dispersion coefficients of six regulated asbestos minerals

Mineral		n_F	n_D	n_C	$n_F - n_C$	Oil used*	References
chrysotile	n_α	1.5563	1.5490	1.5456	0.0107	1.550 (E)	NIST SRM† 1866
	n_γ	1.5649	1.5560	1.5530	0.0119		
grunerite (amosite)	n_α	1.6931	1.6790	1.6734	0.0197	1.680 (B)	NIST SRM 1866
	n_γ	1.7156	1.7010	1.6951	0.0205		
riebeckite (crocidolite)	n_α	1.7132	1.7015	1.6971	0.0161	1.700 (B)	McCrone (1987)
	n_γ	1.7206	1.7072	1.7032	0.0174		
tremolite	n_α	1.6128	1.6063	1.6036	0.0092	1.620 (E)	NIST SRM 1867
	n_β	1.6299	1.6230	1.6201	0.0098		
	n_γ	1.6423	1.6343	1.6310	0.0113		
actinolite	n_α	1.6201	1.6126	1.6095	0.0106	1.625 (E)	NIST SRM 1867
	n_β	1.6369	1.6288	1.6254	0.0115		
	n_γ	1.6485	1.6393	1.6355	0.0130		
anthophyllite	n_α	1.6227	1.6148	1.6116	0.0111	1.625 (E)	NIST SRM 1867
	n_β	1.6350	1.6273	1.6241	0.0109		
	n_γ	1.6449	1.6362	1.6326	0.0123		

* The letter in the parentheses following the numerical values of immersion oils denotes the Series ID used by the manufacturer Cargille Laboratories Inc. See text for details.
† SRM: standard reference materials issued by NIST, Gaithersburg, Maryland.

TABLE 2. Conversion of dispersion staining colors to the corresponding λ_0 (McCrone 1987)

Matching Wavelength (nm)	Particle edge colors* Annular stop‡	Central stop§	Becke line colors† Particle	Liquid
<340	black violet	white	white	–
400	dark violet	pale yellow	pale yellow	–
430	violet	yellow	pale yellow	–
455	blue	golden yellow	yellow	violet
485	blue-green	orange	orange	violet
520	green	red purple	orange-red	violet-blue
560	yellow-green	purple	red-orange	blue-violet
595	yellow	deep blue	red	blue
625	orange	blue-green	faint red	blue
660	red-brown	light blue-green	–	blue-green
700	dark red-brown	pale blue-green	–	pale blue-green
1500	black-brown	very pale blue-green	–	very pale blue-green

* In focus.
† On focusing up.
‡ Observed on a brightfield.
§ Observed on a darkfield.

TABLE 3. Conversion of the matching wavelength λ_0 to the corresponding RI values

Mineral	Chrysotile	Amosite	Crocidolite	Tremolite			Actinolite or Anthophyllite		
Oil $n_D^{25°C}$	1.550	1.660	1.700	1.620	1.610	1.635	1.625	1.610	1.635
Oil Series	E	B	B	E	E	E	E	E	E
RI	n_α or n_γ	n_α or n_γ	n_α or n_γ	n_α or n_γ	n_α	n_γ	n_α or n_γ	n_α	n_γ
λ_0 (nm)									
400	1.579	1.707	1.738	1.651	1.640	1.668	1.654	1.636	1.666
420	1.573	1.702	1.731	1.645	1.634	1.662	1.649	1.632	1.660
440	1.569	1.698	1.725	1.640	1.629	1.657	1.644	1.627	1.655
460	1.565	1.694	1.720	1.636	1.626	1.652	1.640	1.624	1.651
480	1.562	1.691	1.716	1.633	1.622	1.649	1.637	1.621	1.648
500	1.559	1.689	1.712	1.630	1.619	1.645	1.634	1.618	1.645
520	1.557	1.686	1.709	1.627	1.617	1.643	1.632	1.616	1.642
540	1.554	1.684	1.706	1.625	1.615	1.640	1.629	1.614	1.640
560	1.552	1.682	1.703	1.623	1.613	1.638	1.627	1.612	1.638
580	1.551	1.681	1.701	1.621	1.611	1.636	1.626	1.611	1.636
589	1.550	1.680	1.700	1.620	1.610	1.635	1.625	1.610	1.635
600	1.549	1.679	1.699	1.619	1.609	1.634	1.624	1.609	1.634
620	1.548	1.678	1.697	1.618	1.608	1.632	1.623	1.608	1.633
640	1.546	1.677	1.695	1.616	1.606	1.631	1.621	1.607	1.631
660	1.545	1.676	1.694	1.615	1.605	1.630	1.620	1.606	1.630
680	1.544	1.675	1.692	1.614	1.604	1.628	1.619	1.605	1.629
700	1.543	1.674	1.691	1.613	1.603	1.627	1.618	1.604	1.628
720	1.542	1.673	1.690	1.612	1.602	1.626	1.617	1.603	1.627
740	1.542	1.672	1.689	1.611	1.601	1.625	1.616	1.602	1.626
760	1.541	1.671	1.688	1.610	1.600	1.624	1.616	1.601	1.625
780	1.540	1.670	1.687	1.609	1.600	1.623	1.615	1.601	1.624
800	1.539	1.670	1.686	1.609	1.599	1.623	1.614	1.600	1.624
850	1.538	1.668	1.684	1.607	1.597	1.621	1.613	1.599	1.622
900	1.537	1.667	1.682	1.606	1.596	1.619	1.611	1.598	1.621
1000	1.534	1.665	1.679	1.603	1.594	1.617	1.609	1.596	1.618
Δ^L	0.0267	0.0348	0.0370	0.0267	0.0251	0.0291	0.0275	0.0251	0.0291
Δ^s	0.0113	0.0201	0.0166	0.0103	0.0092	0.0113	0.0118	0.0109	0.0127
$\Delta^L - \Delta^s$	0.0154	0.0147	0.0203	0.0164	0.0159	0.0178	0.0157	0.0142	0.0164

Note: Temperature Correction: If oil temperature is not 25 °C, for every 2 °C decrease (increase) in temperature, add (subtract) 0.001 to (from) the listed values.

Conversion of λ_0 to the corresponding RI value

By referring to Table 3, which was calculated from Equation 1, the λ_0 derived from the observed CSDS color can be quickly converted into the corresponding numerical RI value, n_D^s.

The RI values in Table 3 are calculated assuming the liquid or ambient temperature, T, at the time of measurement is 25 °C. If T is not 25 °C, temperature correction should be applied to n_D^t to obtain $n_D^{25°C}$ by using the following equation

$$n_D^{25°C} = n_D^t + (T - 25) \, dn/dt \qquad (2)$$

where dn/dt is the immersion oil's temperature coefficient, a negative value. For practical purposes, the quickest way to apply the temperature correction is to add (or subtract) 0.001 from the Table 3 reading for every 2 °C decrease (or increase) from 25 °C.

Because the Δ^s of actinolite is very close to that of anthophyllite, the two minerals are grouped together. For each asbestos mineral, both n_α and n_γ can be quickly determined with a reasonable accuracy (±0.005 to 0.010) in a single oil mount during routine analysis. However, when higher accuracy is desirable, e.g., when analyzing the Proficiency Testing samples administered by NVLAP, n_α and n_γ can be separately determined using two different oils as suggested in Table 3.

APPLICATIONS TO OTHER RI DETERMINATION TASKS

Although this procedure was designed primarily for the operations of commercial environmental laboratories, its principle can be readily applied to other tasks requiring the determination or screening of the refractive indices of solid particles to improve the efficiency and accuracy of the measurement, especially in the case of completely unknown materials. For details, please see Su (1998). It can also be applied to the determination of the composition of olivine, orthopyroxene, augite, and plagioclase (Su 1994).

APPLICATION OF THE METHOD TO UNKNOWN MATERIALS

The following is an example of measuring the RI of a pure unknown chemical by an operator with minimum experience of dispersion staining technique.

To test how quickly an operator with minimum experience could determine the refractive index of an unknown isotropic material, I gave some powders of NH_4Cl to a technician with one-hour training in comparing refractive index of solid particles against the surrounding immersion oil using both the Becke line and the central stop dispersion staining methods. I told him to start with any oil within the range available in our laboratory, which is 1.400 to 1.750. He chose 1.550 (Series E) because it happened to be on the counter. The colorless powder of NH_4Cl showed high relief and a bright white Becke line that moved into the grain when the distance between the slide and the 10× objective was increased. By checking Table 2, he decided that the matching wavelength λ_0 was approximately 300 nm. Then I told him to use Equation 1 to calculate the RI of this material based on the observed 300 nm matching wavelength, $n_D^L = 1.550$, $\Delta^L = 0.0267$, $k_D = 5.7$, which was calculated from $\lambda_0 = 300$, and $\Delta^S = 0.0084$, which was calculated from the following empirical equation:

$$\log(n_F - n_C) = 5.9 \log n_D - 3.2. \tag{3}$$

Equation 3 was derived by Stoiber and Morse (1994) based on rock-forming mineral data in Tröger (1979). Since the calculated n_D^S was 1.654, the operator chose 1.650 to prepare the second mount of the unknown powder, which showed pale blue-green CSDS color or $\lambda_0 = 700$ nm. Based on the results of the 1.650 preparation, n_D^S was calculated to be 1.542. The operator

chose 1.540 oil for the third preparation and the unknown particles showed a deep blue CSDS color, indicating an exact match between the solid and the liquid at 589 nm, resulting in $n_D^S = 1.540$. Since the temperature of oils were in equilibrium with room temperature 21 °C and the temperature coefficient of 1.550 (E) oil is −0.00042/°C, n_D^S was then calculated to be 1.642. According to Winchell and Winchell (1964), NH_4Cl (salammoniac) has $n_D = 1.6426$.

It should be emphasized that the analyst had only very minimal training and only three oils were used to determine the RI of the unknown isotropic material to an accuracy of ±0.001. My experience is that it usually takes no more than three oils to determine the RI of an unknown material to ±0.003 to 0.005.

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Date: August 12, 2003   SOP No. SRC-LIBBY-05 (Revision 0)

Title: COLLECTION AND ANALYSIS OF ASBESTOS IN INDOOR DUST

Author: William Brattin

SYNOPSIS: A standard method for collecting and analyzing indoor dust samples for asbestos is provided. This method is based on ASTM Method D5755-95, with project-specific modifications intended specifically for use at the Libby Superfund Site.

APPROVALS:

TEAM MEMBER	SIGNATURE/TITLE	DATE
USEPA Region 8	*Joe Goldade*	8/12/03
Syracuse Research Corp.	*W J Bratt*	8/12/03

Revision	Date	Principal Changes
0	08/12/03	--

1.0   PURPOSE

The purpose of this standard operating procedure (SOP) is to provide a standard approach for collection of indoor dust samples and analysis of those samples for asbestos. This SOP is based on ASTM Method D5755-95, with project-specific modifications specifically intended for application at the Libby Superfund site.

2.0   SCOPE AND APPLICATION

This method is intended for preparation and analysis of samples collected for asbestos in indoor dust using ASTM Method D5755-95. This method is appropriate for the preparation and analysis of all types of asbestos fibers, including both chrysotile and amphiboles, including amphiboles that are characteristic of the Libby site

3.0   RESPONSIBILITIES

It is the responsibility of the laboratory supervisor to ensure that all analyses and quality assurance procedures are performed in accord with this SOP, and to identify and take appropriate corrective action to address any deviations that may occur during sample preparation or analysis. The laboratory supervisor should also communicate with project managers at EPA or their oversight contractors any situations where a change from the SOP may be useful, and must receive approval from the EPA Remedial Project Manager or Regional Chemist for any deviation or modification from the SOP before proceeding with sample preparation and analysis.

4.0   METHOD DESCRIPTION

Dust samples are collected in a filter cassette using a microvacuum device. Dust in the cassette is suspended in water and a portion of the suspension is applied to a filter and analyzed for asbestos using transmission electron microscopy (TEM).

5.0   DETAILED METHOD

Dust samples are collected and analyzed in accord with ASTM D5755-95, except for the project-specific modifications, clarifications, and requirements provided below.

1. Sample Collection

Samples will be collected using 25 mm MCE filters. The number of 100-cm² templates collected should be specified in the project-specific plan. In general, a composite of at least three template areas is desired in order to ensure that the sample is representative.

2. Classification of Asbestos Mineral Type

Based on fiber attributes (morphology, SAED, EDXA), asbestos in the sample is classified into one of three categories:

Mineral Class	Description
Libby Amphibole (LA)	Any amphibole asbestos similar to that observed in ores obtained from the mine in Libby. This solution series includes (but may not be limited to) actinolite, tremolite, richterite, and winchite, as well as magnesio-arfedsonite and ferro-edenite.
Other Amphibole (OA)	Other types of amphibole asbestos, including amosite, anthophyllite, and crocidolite. These forms of asbestos are not thought to be related to the mine in Libby.
Chrysotile (C)	Serpentine asbestos. This form of asbestos is the most common type in building materials, and is not thought to be related to the mine in Libby.

A discussion of the EDS spectrum associated with LA fibers is presented in USGS (2002).

3. Secondary Filter Loading

The volume of dust suspension applied to the secondary filter shall be sufficient to produce a total loading of ≤25%.

4. No Structures Detected

In a grid opening where no asbestos structures are detected, enter "ND" (rather than "NSD").

5. Analytical Sensitivity

Target sensitivity is 500 s/cm² or less, with a maximum of 1,000 s/cm². Whenever possible, sensitivity should be controlled by increasing the number of grid openings counted, up to a maximum of 20. If a sensitivity of 1,000 s/cm² cannot be achieved with 20 grid opening, the sample should be ashed in order to reduce debris loading (thereby allowing application of a

larger fraction of the original sample to the secondary filter). If the necessary sensitivity cannot be achieved even after ashing, then the laboratory should complete a laboratory modification form to summarize the issues associated with that sample.

6.0   APPARATUS AND MATERIALS

All equipment and materials are as described in ASTM D5755-95.

7.0   QUALITY ASSURANCE/QUALITY CONTROL

All QA/QC procedures are as described in ASTM D5755-95, except for the project-specific modifications, clarifications, and requirements provided below.

1.   Field Blanks

Field blanks will be collected at a rate of one per sample team per day. The EPA regional chemist will specify the fraction of field blanks that must undergo analysis, as documented in a modification form LFO-000064. In the absence of any evidence of contamination, the rate will typically be one sample per team per week.

2.   Re-Analysis

Each laboratory will prepare and analyze up to five different types of QC sample at the rates specified in Mod LB-000029.

8.0   RECORDS

8.1   Data Forms

Analysts will record analytical results using the electronic data sheets developed for the Libby project, as presented in the Dust Sampling and Analysis Plan (SAP). Once completed and checked, these spreadsheets are submitted to EPA for upload into the database. The laboratory should retain all original records for use in resolving any questions until otherwise instructed by EPA.

8.2   Instrument Maintenance Logbook

An individual instrument maintenance logbook should be kept for each piece of equipment in use at the laboratory. All maintenance activities must be recorded in the appropriate logbook.

8.3   Data Storage and Archival

Electronic Data. Each day of data acquisition, all electronic files will be saved onto two separate media. For example, the data may be saved onto a computer hard drive, but must also be backed up onto a type of portable media such as CD-ROM, floppy disc, or tape. Portable media will be maintained in a single location with limited access.

Hardcopy Data. All data sheets and micrographs must be stored in a secured location with limited access (e.g., locking file cabinet) when not in use.

Copies (hardcopy and electronic) of the raw analytical data will be submitted to USEPA for archival.

9.0   REFERENCES

ATSM. 1995. Standard Test method for Microvacuum Sampling and Indirect Analysis of Dust by Transmission Electron Microscopy for Asbestos Structure Number Concentrations. American Society of Testing and Materials. Method Designation D 5755-95. October, 1995.

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Libby Standard Operating Procedure
Approved for Use at the Libby Superfund Site Only
Analysis of Asbestos in Dustfall Samples by TEM (Revision 0)

Date: 05/04/05   SOP No. SRC-LIBBY-07

Title: <u>ANALYSIS OF ASBESTOS IN DUSTFALL SAMPLES BY TEM</u>

Author: <u>Amber Graves</u>   Syracuse Research Corporation

SYNOPSIS: A standardized method is presented for measuring asbestos concentrations in dust released to air during site cleanup activities such as soil removal or building demolition. This method is adapted from methods ASTM D5755-95 and ISO 10312.

Received by QA Unit:

APPROVALS:

TEAM MEMBER	SIGNATURE/TITLE	DATE
EPA Region 8		
Syracuse Research Corp.		

Revision	Date	Reason
0	05/04/2005	--

Libby Standard Operating Procedure
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Analysis of Asbestos in Dustfall Samples by TEM (Revision 0)

1.0   PURPOSE

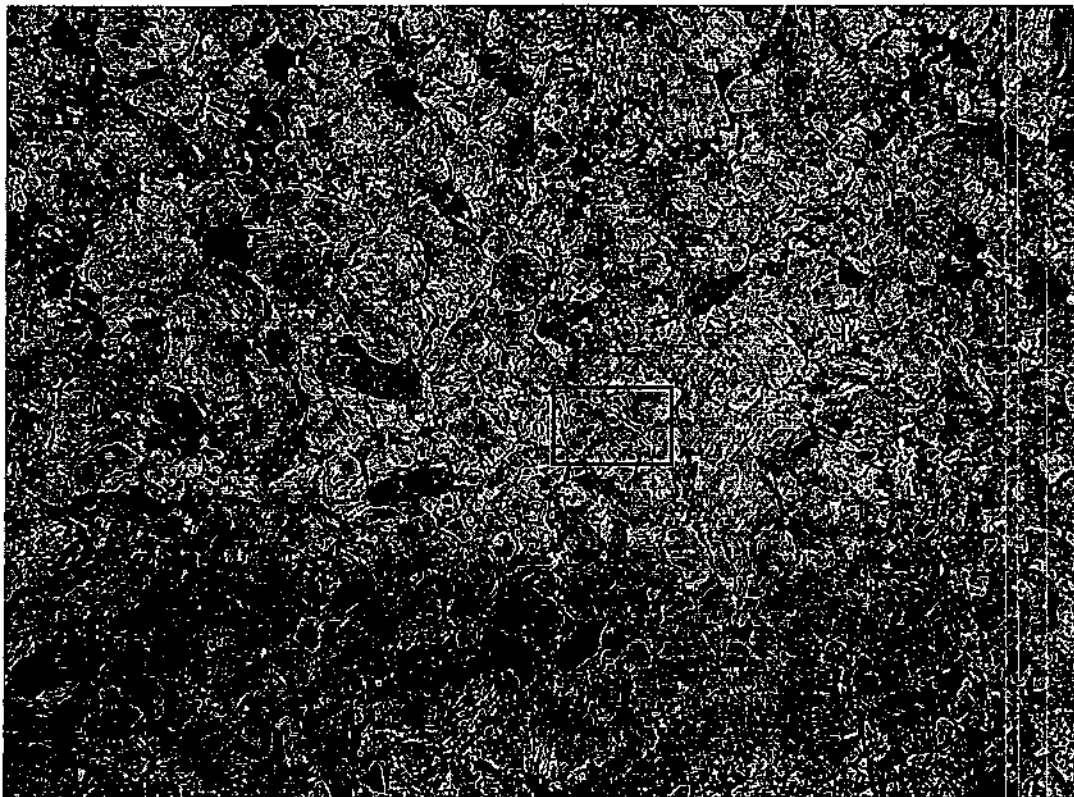The purpose of this Standard Operating Procedure (SOP) is to provide a standardized method for transmission electron microscope (TEM) analysis of asbestos in samples of dust collected by a passive fallout collector as described in SOP SRC-LIBBY-06. This procedure is intended for use by employees of USEPA Region 8 and by contractors and subcontractors supporting USEPA Region 8 projects and tasks for the Remedial Investigation work performed at the Libby, Montana, Superfund site.

2.0   RESPONSIBILITIES

The Laboratory Director is responsible for ensuring that fallout samples provided to the laboratory for evaluation are handled and evaluated in accord with the requirements of this SOP, and for communicating to the appropriate USEPA Region 8 Remedial Project Manager or Regional Chemist any recommended changes or proposed improvements to the SOP.

3.0   EQUIPMENT

- Filtered, deionized (FDI) water - sample suspension medium
- Clean 500 mL graduated cylinder
- Filter apparatus, glass or disposable
- 25-mm or 37-mm diameter cellulose ester (MCE) filters with 0.45 um or smaller pore size
- Tweezers - MCE filter preparation for TEM
- Scalpel blade - MCE filter preparation for TEM
- Dimethylformamide/acetic acid mixture - MCE filter preparation for TEM
- Micropipette with disposal tips - MCE filter preparation for TEM
- Plasma etcher -MCE filter preparation for TEM
- Carbon coater - MCE filter preparation for TEM
- Jaffe washer - MCE filter preparation for TEM
- Acetone vapor generator- MCE filter preparation for TEM
- TEM- 80 to 120 kV transmission electron microscope (TEM), capable of performing electron diffraction with a fluorescent screen inscribed with calibrated gradations, is required. The TEM must be equipped with energy dispersive X-ray spectroscopy (EDS) and it must have a scanning TEM (STEM) attachment or be capable of producing a spot size of less than 250 nm in diameter in crossover. The microscope must be calibrated and maintained according to the requirements described in NVLAP Airborne Asbestos Program.

4.0   METHOD SUMMARY

Samples of dust fallout will be provided to the laboratory in capped collection cylinders that are about 6 inches in diameter and about 12 inches tall. The cylinders will contain a

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layer of water in the bottom to help ensure that all particles which entered the cylinder are retained. At the laboratory, the contents of the cylinder will be collected onto an MCE filter by vacuum filtration. This filter is then prepared and examined for asbestos structures by TEM in basic accord with ISO 10312. The units of the results may be expressed either as total asbestos fallout (s/cm^2) or as a rate of fallout (s/cm^2/hr).

5.0   SAMPLE PREPARATION AND ANALYSIS

5.1   Sample Filtration

Pour the water from the collection cylinder into a clean 500-mL graduated cylinder. Rinse the container thoroughly with FDI water and collect the rinsate in the graduated cylinder. Add additional FDI water to a final volume of 500 mL. Thoroughly mix the 500 mL sample by hand-inverting 10 times.

Remove 250 mL of the sample suspension and filter through a 25 mm or 37 mm MCE filter (0.45 um or smaller pore size) using a disposable filter funnel. If the dust loading on the filter is too heavy, prepare a second filter using a smaller volume.

5.2   TEM Filter Preparation

Prepare at least two grids from the filter for examination by TEM in accord with the standard methods described in International Organization for Standardization (ISO) method 10312, except where specifically indicated in this method or where appropriate project-specific laboratory modifications are necessary.

5.3   Counting Rules

Counting rules are the same as described in ISO 10312, except that all asbestos structures 0.5 um in length and with an aspect ratio of at least 3:1 should be recorded. Target sensitivity and appropriate stopping rules should be specified in the workplan or QAPP/SAP developed for the project.

6.0   COMPUTATION OF RESULTS

The amount of asbestos in dust fallout during a sampling period is calculated using the following equation:

$$AFO = \frac{N \cdot EFA}{GO \cdot Ago \cdot A \cdot F}$$

where:

    AFO   = Asbestos fallout (structures / cm^2)
    N   = Number of countable asbestos structures observed
    EFA   = Effective filter area (mm^2)

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GO = Number of grid openings examined
Ago = Area of one grid opening (mm^2)
A   = Area of collection cylinder (cm^2)
F   = Fraction of original sample applied to filter

If the number of asbestos structures observed is zero, the results should be reported as less than the analytical sensitivity , where sensitivity is given by:

$$S = \frac{EFA}{GO \cdot Ago \cdot A \cdot F}$$

For convenience, all of these calculations are performed automatically by the electronic analytical data recording sheet (Attachment 1).

Asbestos fallout rate (AFR) is computed from AFO as follows:

AFR = AFO / Collection time (hr)

7.0 QUALITY ASSURANCE

Laboratory blanks should be prepared and analyzed in accord with standard laboratory practice. If asbestos contamination is detected on a laboratory blank sample, the laboratory director should take immediate steps to identify and address the source of the contamination before any further field samples are analyzed.

8.0 DOCUMENTATION

All analytical results for each sample should be recorded using the standard electronic data sheet provided in Attachment1.

9.0 REFERENCES

American Society for Testing and Materials. 1995. Standard Test method for Microvacuum Sampling and Indirect Analysis of Dust by Transmission Electron Microscopy for Asbestos Structure Number Concentrations. ASTM Method D 5755-95.

International Organization for Standardization. 1995. Ambient air -- Determination of Asbestos Fibres -- Direct Transfer Transmission Electron Microscopy Method. ISO Method 10312.

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ATTACHMENT 1

Electronic Datasheet for Recording Analytical Results

TEM.xls
(Check with Volpe or SRC to determine the most recent version number)

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Research Method for Sampling and Analysis of Fibrous Amphibole in Vermiculite Attic Insulation

TABLE OF CONTENTS

1   INTRODUCTION AND BACKGROUND

1.1   General

The purpose of this procedure is to provide the U. S. Environmental Protection Agency's (EPA) Office of Research and Development (ORD) with a method for the characterization of the fibrous amphibole content of vermiculite attic insulation (VAI). This procedure is to be used in an ORD research project dealing with determining the airborne levels of fibrous amphiboles in residences where VAI is used. This procedure was developed from input received from fibrous amphibole monitoring experts at an interagency meeting on "Analytical Method for Bulk Analysis of Vermiculite," held in Greater Cincinnati, Ohio on July 17-18, 2003. This procedure was developed from a method prepared by Eric J. Chatfield, Ph.D., Chatfield Technical Consulting, Inc., Mississauga, Ontario, Canada, for Mr. Wayne Toland, U.S. Environmental Protection Agency, EPA Region 1, Boston, MA, 02114. The current method has streamlined the original method to provide a means for analytical laboratories to determine the presence of fibrous amphiboles in VAI. For analysis of vermiculite in other materials, the analyst is referred to the original method by Chatfield, [Chatfield (2000)].

This method provides an approach to determine the percentage of fibrous amphibole present in VAI. EPA is determining this percentage for purposes of selecting residences to sample during the research project. EPA does not correlate the percentage of fibrous amphibole, as determined by this method, with risk or remediation. While the principles of this procedure may be applied to the analysis of other vermiculite materials, it may be necessary for the user to address any unique characteristics of these alternate materials with appropriate modifications to this procedure.

Vermiculite is a naturally occurring mineral that has the unusual property of expanding into "books" or worm-like accordion shaped pieces when heated. The expanded vermiculite is a light-weight, fire-resistant, absorbent, and odorless material. These properties allow vermiculite to be used in numerous applications, including attic insulation. Sizes of vermiculite products range from very fine particles to large (coarse) pieces nearly an inch in dimension. Vermiculite attic insulation (VAI) is a pour-in product, fragments of which are generally approximately 5 mm to 1cm in dimension, and is usually light-brown or gold in color. An example of VAI is shown as Figure 1 as well as on the cover of this document. The object highlighted by the black box in the cover photo is a large fragment of fibrous amphibole which is grey in color.

As is the case for most minerals, deposits of vermiculite usually contain other mineral phases, many of which are removed during processing. The process by which vermiculite is concentrated from the crude ore is referred to as beneficiation. During beneficiation of crude vermiculite ore, the vermiculite is also segregated into different size fractions for different applications. Larger sizes of vermiculite flakes command a higher price.

Vermiculite from Vermiculite Mountain (also called Zonolite Mountain) near Libby, MT is likely to contain fibrous amphibole. This fibrous amphibole displays a continuum of

1
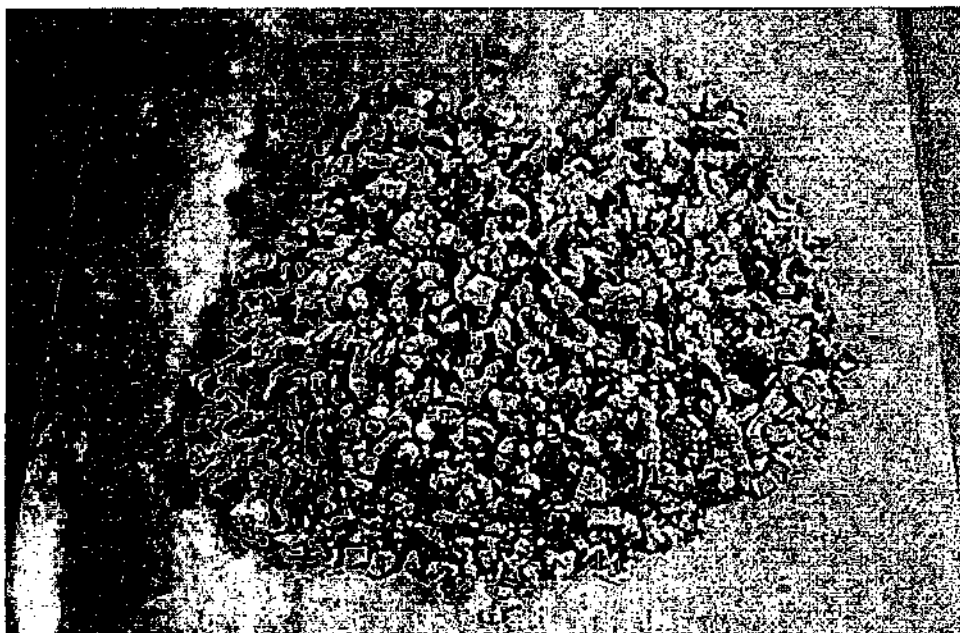
Figure 1. Example of Exfoliated Vermiculite Attic Insulation
(Photo by E. J. Chatfield)

morphologies from acicular to asbestiform. Vermiculite from other sources may or may not contain fibrous amphibole. During the beneficiation the fibrous amphibole may, to a large extent, be removed from the vermiculite. However, some of the fibrous amphibole, if present, may pass through the beneficiation process and appear in the final vermiculite product.

Assuming that amphibole fragments are present in the beneficiated vermiculite, the amount of amphibole present in the final exfoliated product depends on the practices of the exfoliation facility. During exfoliation, the vermiculite expands to 5 - 15 times its original volume, and these very light fragments are separated by air entrainment. The other minerals present in the original beneficiated vermiculite are not useful, and represent material (usually referred to as "rock") that must be disposed of by the exfoliation facility. Some facilities return the "rock" to the vermiculite after the exfoliation process, and it is therefore incorporated into the final product. Other facilities dispose of the "rock" as a waste material. The importance of this to the analyst is that non-vermiculite fragments may be common in some samples but relatively rare in others.

1.2 Required Characteristics for an Analytical Method for Determination of Fibrous Amphibole in Vermiculite Attic Insulation

This method assumes that Vermiculite Attic Insulation (VAI) is normally used as purchased, and is not ground or pulverized to a powder.

This analytical method incorporates a procedure by which fibrous amphibole can be separated from the bulk material, without generating additional fine fibers by crushing or grinding of the material. Neither scanning electron microscopy (SEM) nor transmission electron microscopy (TEM) is an appropriate method for determination of the weight percent fibrous amphibole in vermiculite, because the size range of fiber bundles of fibrous amphibole that may be present in vermiculite extends up to approximately the dimensions of the vermiculite flakes, and the majority of the weight of fibrous amphibole is represented by these larger fiber bundles that are very much larger than can be examined by SEM/TEM. Any attempt to measure the weight concentration by SEM/TEM will usually yield a value that significantly under-estimates the actual concentration. However, SEM/TEM is an appropriate method for determination of the numerical concentration of fine fibers. This analytical method incorporates a procedure by which fine fibers can be separated from the vermiculite, without generating additional fine fibers by crushing or grinding of the material.

It is most important to recognize that reliable and reproducible results cannot be obtained by analysis of small quantities of samples. Any amphibole particles present in vermiculite are usually much fewer in number than the flakes of vermiculite, and if only a small sample size is analyzed the number of amphibole particles included in the sample will be small and often unrepresentative.

1.3 Analytical Considerations Specific to Vermiculite from Libby, Montana

Prior to 1990, a large proportion of the U.S. consumption of vermiculite originated from the mine at Libby, Montana. Depending on the date of production, beneficiated vermiculite from Libby may have contained several percent of fibrous amphibole, down to a fraction of a percent shortly before the mine was closed in 1990.

From an analytical perspective, it is important to recognize that, with relatively simple, but appropriate, analytical procedures specified in this method, the fibrous amphibole in vermiculite from the Libby mine can be readily recognized and the weight percent of fibrous amphibole can be estimated in the range of less than approximately 0.01% to several percent by weight. This measurement can be made using conventional chemical laboratory equipment, a stereo-binocular microscope and a polarized light microscope. Samples of vermiculite attic insulation that originated from the Libby mine will generally yield sufficient fibrous amphibole to determine the approximate weight concentration by weighing.

(a) Rapid Screening Procedure for Sinks Fraction ("Sinks")

The weight percent fibrous amphibole is determined by separating fibrous amphibole from VAI and weighing it. A known weight of the VAI is first suspended in water. Most of the vermiculite floats to the top of the suspension, and this vermiculite is removed and saved for possible further examination. After allowing time for most of the suspended material to settle, the water is decanted and saved, and the sediment is dried and weighed. The dried sediment is examined under a stereo-binocular microscope. If there is more than approximately 0.01% of fibrous amphibole in the original sample, the fiber bundles are readily recognized during the stereo-microscope examination, and it is possible to hand-pick these fiber bundles from the sediment and weigh them. Representative fibrous amphibole particles are identified by PLM, SEM-EDS or TEM-EDS.

(b) Procedure for "Suspended Particles Fraction."

If no fibrous amphibole is detected in the sediment, the suspended particles fraction saved from the wash above, is analyzed. *This suspension should be filtered within 24 hours of the washing in order to minimize bacterial growth in the sample.* Aliquots of the suspension are filtered through membrane filters, and TEM specimens are prepared from the filters. The TEM specimens are examined, and fibers are identified and their dimensions are recorded. Alternately, the sample may be prepared and analyzed by SEM. The balance of the suspension is filtered on to a pre-weighed membrane filter. The filter is dried and weighed to obtain the total weight of suspended particles.
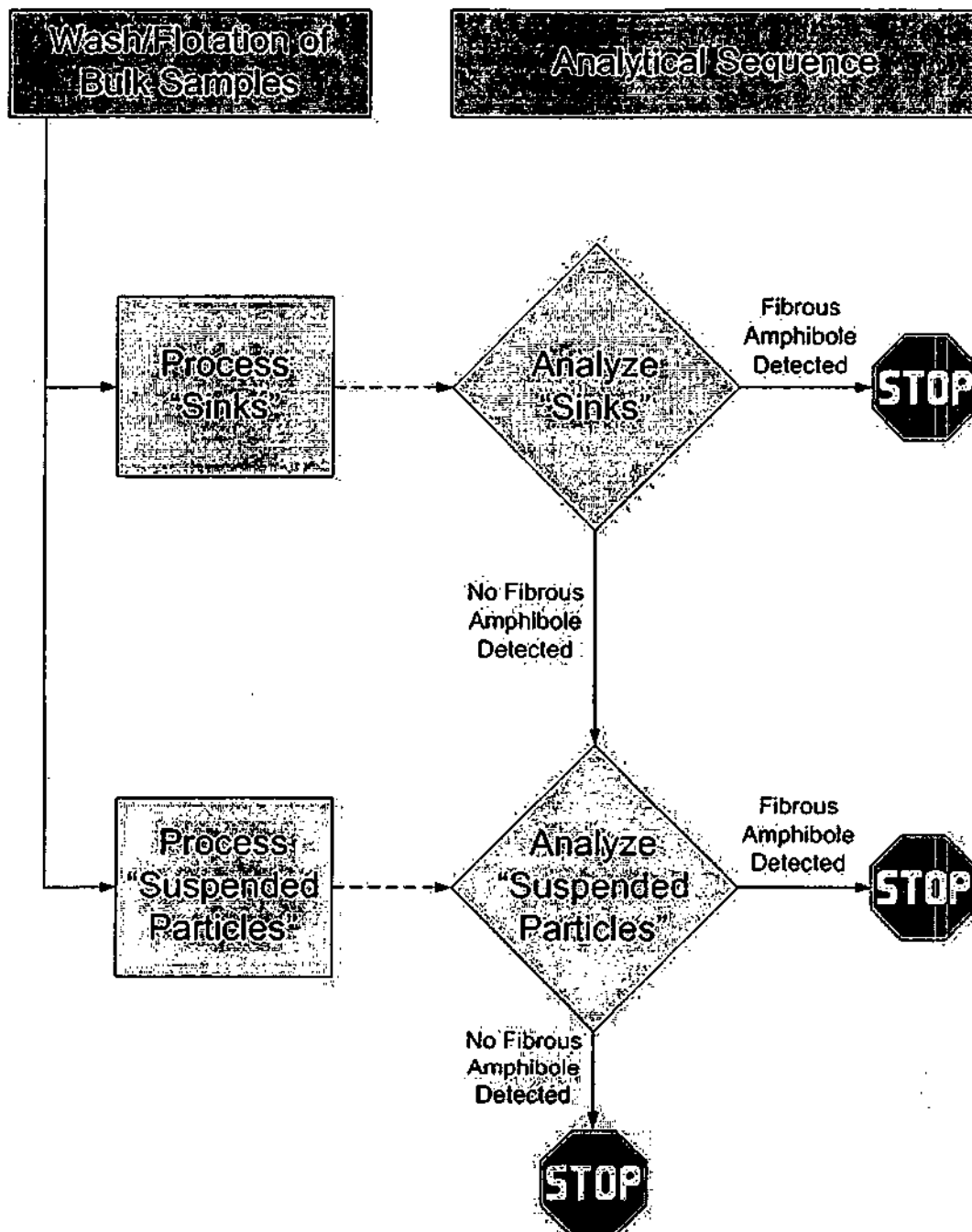
Figure 2. Analytical Sequence Flow Chart

3   SCOPE AND FIELD OF APPLICATION

3.1   Substance determined

3.1.1   Weight Percent Fibrous Amphibole

The rapid screening method specifies a procedure to determine the weight percent of fibrous amphibole.

3.1.2   Numerical Concentration of Suspended Amphibole Fibers

The method specifies a TEM or SEM procedure to determine the concentration of suspended fibrous amphiboles in VAI. The concentration of suspended fibrous amphiboles is expressed as the numerical concentration per gram of sample. The lengths, widths and aspect ratios of the fibers and bundles are measured. The method allows determination of the type(s) of fibers present. As for all routine TEM/SEM analytical methods, this method cannot always discriminate between an individual fiber of the fibrous and non-fibrous analogues of the same amphibole mineral.

3.2   Type of Sample

The method is defined for samples of vermiculite attic insulation.

3.3   Range

The range of fibrous amphibole weight concentration that can be measured is estimated to be approximately 0.01% to 100%.

The minimum suspended particle concentration that can be measured is dependent on the volume of the suspension that can be filtered while still yielding filters that are appropriately-loaded for preparation of TEM/SEM specimens. The minimum for the suspended particle concentration can be lowered by examination of a larger area of the TEM/SEM specimens. There is no maximum, since the analytical parameters can always be adjusted to accommodate high fiber concentrations.

3.4   Limit of Detection

For the rapid screening method, the limit of detection for fibrous amphibole is estimated to be less than approximately 0.01% by weight.

Theoretically, for determination of the concentration of suspended particles, the limit of detection can be lowered indefinitely by increasing the volume of liquid filtered during specimen preparation, and by increasing the area of the TEM/SEM specimens examined in the electron

microscope. In practice, for a particular area of TEM/SEM specimens examined, the lowest achievable limit of detection is controlled by the total amount of particulate material in the suspended particle size range. There is an upper limit to the volume of the final suspension that can be filtered, if TEM/SEM specimens of appropriate particulate loading are to be obtained. Lower limits of detection can be achieved by increasing the area of the TEM/SEM specimens that is examined. In order to achieve lower limits of detection for fibers and bundles longer than 5 μm, and for PCM equivalent fibers (fibers detected under TEM/SEM that would be expected to also be seen by Phase Contrast Microscopy techniques: usually fibers greater than 5 um in length, and greater than 0.25 um in width.), lower magnifications are specified which permit more rapid examination of larger areas of the TEM/SEM specimens when the examination is limited to these dimensions of fiber.

4   DEFINITIONS

Amphibole: A group of rock-forming ferromagnesium silicate minerals, closely related in crystal form and composition, and having the nominal formula:

$$A_{0-1}B_2C_5T_8O_{22}(OH,F,Cl)_2$$
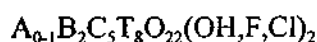
where the most common constituents are:

$$A = K, Na;$$

$$B = Fe^{2+}, Mn, Mg, Ca, Na;$$

$$C = Al, Cr, Ti, Fe^{3+}, Mg, Fe^{2+};$$

$$T = Si, Al, Cr, Fe^{3+}, Ti.$$

Amphibole is characterized by a cross-linked double chain of Si-O tetrahedra with a silicon:oxygen ratio of 4:11, by columnar or fibrous prismatic crystals and by good prismatic cleavage in two directions parallel to the crystal faces and intersecting at angles of about 56° and 124°.

Analytical filter: A filter through which an aqueous suspension of particles is passed, and from which TEM/SEM specimen grids are prepared.

Asbestiform: Aggregates of long, thin, flexible mineral particles resembling organic fibers that occur in significant quantity and quality to be economically useful.

Aspect ratio: The ratio of length to width of a particle.

Beneficiation: The process in which vermiculite is concentrated from the crude ore and separated into different size fractions.

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Filter Blank: A structure count made on TEM/SEM specimens prepared from an unused filter, to determine the background measurement.

Cleavage: The breaking of a mineral along specific crystallographic directions.

Cleavage fragment: A broken fragment of a larger crystal that is predominantly bounded by cleavage faces.

Cluster: A structure in which two or more fibers, or fiber bundles, are randomly oriented in a connected grouping.

Energy dispersive X-ray spectroscopy (EDS): Measurement of the energies and intensities of X-rays by use of a solid state detector and multi-channel analyzer system.

Exfoliation: A process in which vermiculite flakes are expanded by sudden heating or by chemical action.

Fibril: The smallest structural unit of a fiber bundle.

Fibrous: The tendency of certain minerals to crystallize in needle-like grains or fibers, including the asbestiform habit.

Fiber (countable): Fiber (countable): For this method a countable fiber is defined as an elongate particle with a minimum aspect ratio of 3:1.

Fiber (mineral): An elongate particle or parallel group of elongate particles. On average in a population of fibers, the lengths of fibers are much greater than their widths (over ten times). Note that for different fiber count methods, the minimum aspect ratio (the relationship between the length and width) used to define a fiber may vary. Fiber morphologies can include acicular (needle-like) and asbestiform.

Fiber bundle: A structure composed of parallel, smaller diameter fibers attached along their lengths. A fiber bundle may exhibit diverging fibers at one or both ends.

Fibrous structure: A fiber, or connected grouping of fibers, with or without other particles.

Fine fiber: A fiber of aspect ratio greater than or equal to 3:1, longer than 5 μm.

Funnel blank: A structure count made on SEM/TEM specimens prepared by the direct-transfer method from a filter used for filtration of a sample of distilled water.

Habit: The characteristic crystal growth form or combination of these forms of a mineral, including characteristic irregularities.

6   EQUIPMENT AND APPARATUS

6.1   General

General laboratory equipment, such as glass beakers, disposable pipets, disposable plastic beakers and measuring cylinders, is required, with the addition of the specific items listed below. Some analyses do not require all of the equipment listed.

Note: *Additional reagents and equipment are listed in the referenced TEM and SEM preparation methods.*

6.2   Sampling

6.2.1 Scoop, metal (approximately 12 by 5 cm) with a flat edge

6.2.2 One gallon plastic resealable bags

6.2.3 Sample labels and markers

6.2.4 Chain-of-custody forms

6.3   Sample preparation

6.3.1 Laboratory balance, sensitivity 0.0001 gram

6.3.2 Laboratory magnetic stirrer

6.3.3 Teflon coated magnetic stirrer bars

6.4   Rapid Screening Method for "Sinks Fraction" by Stereomicroscopy/PLM

6.4.1 Water aspirator

6.4.2 Stereo-binocular microscope, 10x to 40x magnification

6.4.3 Polarized light microscope

6.4.3 Drying oven, capable of drying samples at 100° C

6.4.4 Desiccator, cabinet type for drying filters

have settled in the VAI, will be sampled. A minimum of three 1-gallon samples are recommended for each sampling site.

Vermiculite attic insulation may have a substantial water content, and so all samples shall be dried at 100° C for 2 hours and until the sample reaches constant weight before analysis. The sample shall be weighed before and after drying to obtain the weight of water, so that the final results can be expressed in terms of the original weight or dry weight of the sample.

8.3   Obtaining a Representative Sub-Sample for Analysis

If amphibole is present in VAI, the size range of the fragments of amphibole is usually approximately the same as that of the vermiculite flakes, because during the beneficiation process the material is segregated into several different size categories. The fragments of amphibole are distributed randomly throughout the VAI, and the number of these fragments is generally much lower than the numbers of vermiculite flakes. Accordingly, if a reproducible analysis is to be obtained, it is necessary to select a sub-sample of VAI sufficiently large that a statistically-valid number of the amphibole fragments are included. The weight of sub-sample required for analysis is dependent on the size grade of the vermiculite. Table 1 gives recommended approximate weights **of vermiculite** that should be used for the initial sub-sample. For products such as VAI, the material is likely to be primarily vermiculite and the weights given in Table 1 will generally apply. If additional materials have been added to or have contaminated the VAI, a visual estimate of the proportion of vermiculite in the product should be made and the starting weights in Table 1 should be proportionately increased.

Table 1. Recommended Sub-Sample Weights of Vermiculite for Analysis

Size of Vermiculite Flakes, mm	Recommended Minimum Sub-sample Weight for Analysis, grams
<2	5
>2 - <5	10
>5	50

The sub-sample shall be obtained from the original sample by the cone and quarter method. On a clean surface, such as a sheet of aluminum foil, form the sample into a cone. Using a thin flat sheet of metal or rigid plastic, divide the cone into two parts, vertically from the apex. Form either of the two fractions into a cone, and repeat the procedure until one of the separate fractions is of a suitable weight for analysis.

wash portions of the vermiculite in this manner until all of the sub-sample (weighed according to Table 1) has been treated. Carefully remove all fragments of vermiculite from the surface of the water, and allow the suspension to settle for 60 minutes. After this period of time, any amphibole fibers thicker than approximately 3 μm will have settled to the bottom of the beaker. Using a pump or syphon, transfer the supernatant liquid to a second beaker. Using ethanol, wash the sediment from the first beaker into a glass petri-dish and dry the sediment by placing the petri-dish on a slide warmer at a temperature of approximately 60°C. Use of an oven for drying the sediment is not recommended, because of the hazards associated with evaporation of ethanol in a closed environment. Transfer the sediment to a pre-weighed dish, and weigh the dish to obtain the weight of the sediment. Figure 4 shows an example of sediment after the water sedimentation procedure.

9.2.3 Optional Preparation of SEM/TEM Specimens From the Suspended Particles Fraction

If fibrous amphibole is detected visually in the sediment from the wash liquid, it can be assumed that suspended amphibole fibers are present in the suspended particles fraction. If fibrous amphibole is not detected visually in the wash liquid, there is still a possibility that suspended particles of amphibole fibers, too small for detection visually or by the stereo binocular microscope and PLM, could be present. This possibility can be confirmed or discounted by examination of particles in the aqueous suspension by SEM/TEM. Prepare analytical filters by the procedure described in 9.3.3. It is beyond the scope of this document to describe the preparation of TEM specimens from membrane filters; these procedures are fully described in ISO 13794.

9.2.4 Stereo-Binocular Microscope Examination of the "Sinks"

The "sinks" will contain particles large enough to detect with a stereo-binocular microscope. The "sinks" will include any large amphibole particles present in the original sub-sample. There are three possible outcomes which define the extent to which further analytical work on these "sinks" is necessary. The procedure shall be either (a), (b) or (c).

(a) If the sample originated from Libby, Montana, the "sinks" will likely contain a major proportion of large fiber bundles that are gray-green in color, and are easily visible under the stereo-binocular microscope at magnifications up to 40x. If a sub-sample of sufficient size was used, numerous fiber bundles should be present in the "sinks", as shown in Figure 3. The analyst will generally have no difficulty recognizing these fiber bundles. There are two options for determining the weight of fiber bundles in the "sinks," use forceps to: (1) move the fiber bundles into another previously weighed empty vessel and weigh them; or (2) remove non-fiber bundles from the sinks and weigh the remaining "fiber-bundle sinks." The analyst must determine which will be the more efficient approach. The fiber bundles picked from such "sinks" are shown in Figure 4. After the fiber bundles have been weighed, representative bundles shall be selected for identification by either PLM, SEM or TEM. The morphology, color and optical properties of the fibrous amphibole in vermiculite originating from
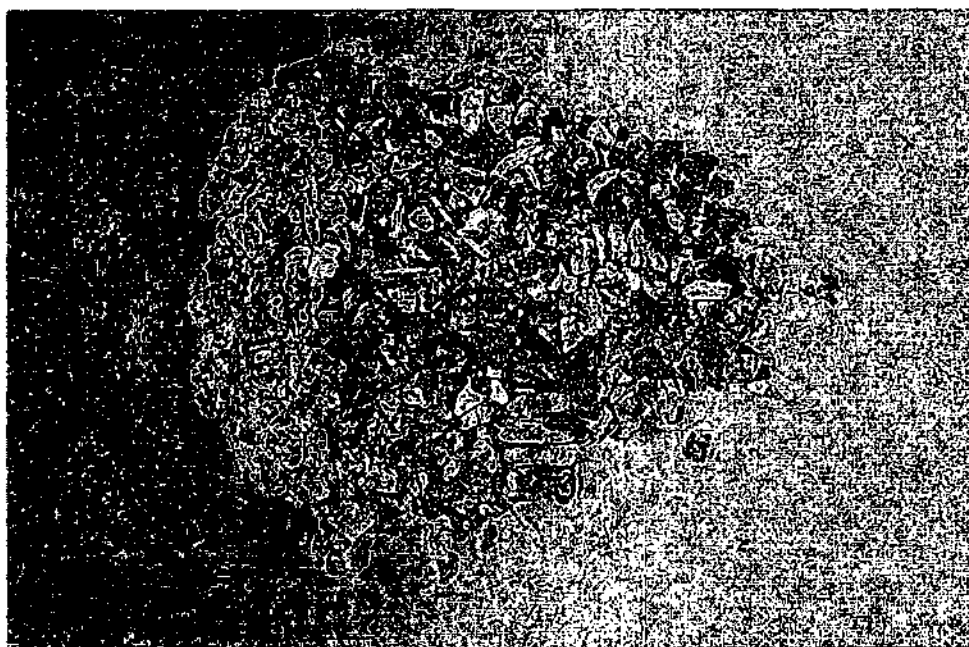
Figure 3. Example of Sediment or "Sinks" After Flotation of VAI
(Photo by E. J. Chatfield)

Libby are characteristic (Bandli and Gunter, 2001) (Wylie and Verkouteren, 2000), and with experience, the analyst need go no further than mounting representative fiber bundles in a high dispersion liquid of refractive index 1.630, in which the very fine fibers exhibit dispersion staining colors of magenta to gold (parallel) and blue (perpendicular). Representative fiber bundles may be examined by SEM or TEM, and the EDS spectra obtained may be used as the basis for identification. Examples of EDS spectra for Libby amphiboles are shown in Appendix A.

(b)   If the sample originated from a mine other than Libby, Montana, few fibrous amphibole bundles, if any, may be observed in the "sinks" during the stereo-binocular microscope examination. However, the "sinks" may contain a large proportion of non-fibrous amphibole fragments. An example of these fragments is shown in Figure 5. Non- fibrous amphibole fragments are prismatic and may have crystal faces intersecting at angles of approximately 56° and 124°. In well-crystallized material, these angles can be recognized by examination of the ends of elongated fragments, such as shown in Figure 5. The total amount of non-fibrous amphibole may be estimated by hand-picking of fragments and weighing, using the same

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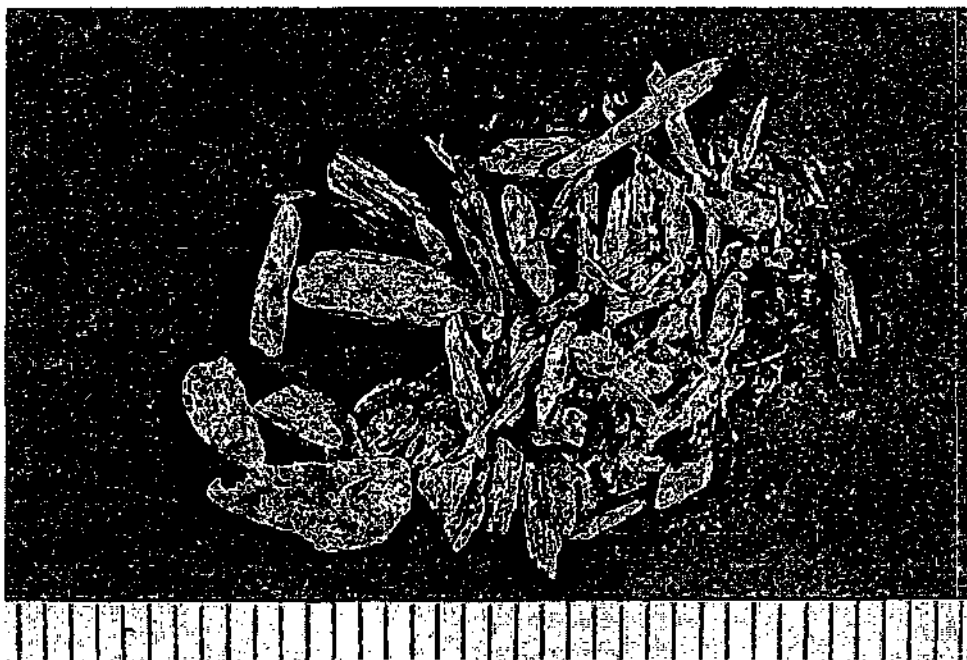
Figure 4. Fibrous Amphibole Bundles Hand-Picked from Sinks after Flotation of VAI which Originated from Libby, MT.
(Scale divisions = 1 mm, Photo by E. J. Chatfield)
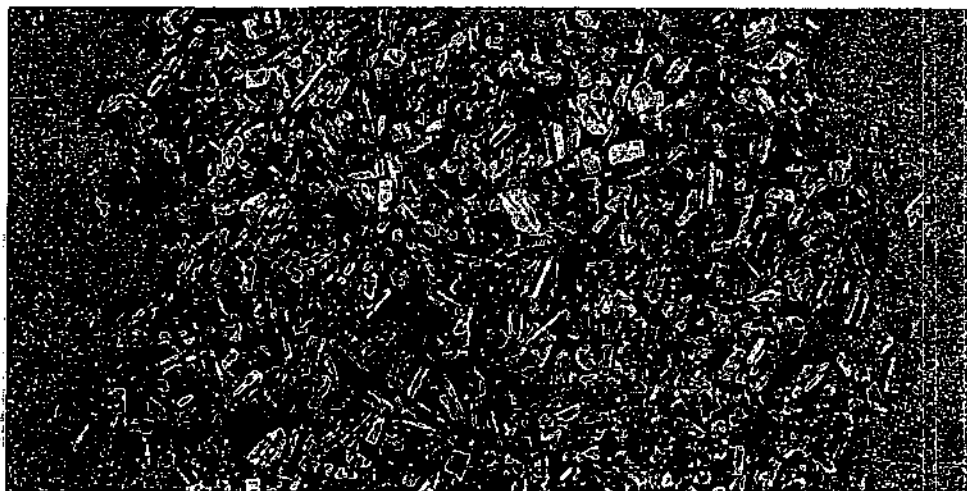
Figure 5. Example of Non-Fibrous Tremolite Detected in a Vermiculite Sample
(Photo by E. J. Chatfield)

9.3 Determination of Concentration of Suspended Fibrous Amphibole Particles by Electron Microscopy

9.3.1 Introduction

In this procedure, the suspended particles fraction saved from Section 9.2.2 is analyzed. SEM/TEM specimens are prepared from aliquots taken from the suspension, and the balance of the suspension is filtered through a pre-weighed filter. After drying, the filter is weighed to determine the total weight of suspended particles. Readily-available laboratory apparatus is used to perform this measurement.

9.3.2 Separation of Suspended Particles

After all of the floating vermiculite has been removed and the suspended particles fraction decanted from the "sinks," make the suspension up to a volume of 1 liter using reagent water. Place the beaker into a calibrated ultrasonic bath for 2 minutes. Remove the beaker from the ultrasonic bath, and mix the contents by air bubbling using filtered air.

9.3.3 Preparation of SEM/TEM Specimens From "Suspended Particles Fraction"

Filtration of the aqueous suspension is a very critical procedure because it is important to obtain uniform deposits of particulate on the analytical filters. The following procedure shall be used.

(a)   Set up the filtration system and connect to a vacuum source;

(b)   Add freshly distilled water to the filtration unit base component until there is a raised meniscus;

(c)   Place a 5 μm pore size cellulose ester filter on to the water meniscus. The filter will centralize. Apply the vacuum very briefly in order to bring the filter into contact with the base component;

(d)   Add freshly distilled water to the top of the cellulose ester filter, and place the analytical filter (either a 0.2 μm maximum pore size capillary-pore polycarbonate filter or a 0.22 μm maximum pore size cellulose ester filter) on to the water surface. Apply the vacuum very briefly again in order to bring both filters into contact with the base component;

(e)   Install the filtration reservoir and clamp the assembly together.

(f)   Before filtering the aqueous suspensions, prepare a funnel blank by filtration of 40 mL of freshly-distilled water. This sample is a control to ensure that the filtration equipment is clean and the reagent water is not contaminated by fibers.

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(g) The volume of the aqueous suspension to be filtered depends on either the particulate concentration or the amphibole fiber concentration. The volume of the aqueous suspension required to produce an analytical filter with a suitable particulate or fiber loading for analysis often cannot be predicted, and it is usually necessary to prepare and examine several analytical filters corresponding to filtration of different aliquots. The number of grid openings on the TEM specimens that require examination in order to achieve a particular analytical sensitivity are shown in Table 2.

(h) The aqueous suspensions are generally not stable; it is therefore necessary to prepare all analytical filters immediately. Uniform deposits of particulate on the analytical filters cannot be assured if liquid volumes smaller than 5 mL are filtered using filtration systems of 199 mm^2 active area; accordingly, where it is required to filter volumes smaller than 5 mL, the aliquot shall be diluted with freshly-distilled and filtered water to a volume exceeding 5 mL.

(i) Pour the aliquot of the suspension into the filtration reservoir, and apply the vacuum. If the volume of the aliquot is larger than the capacity of the filtration reservoir, do not allow the level of liquid in the reservoir to fall below 5 cm depth before the remaining volume is added. Failure to observe this precaution may result in disturbance of the filtered particulate and non-uniform deposition.

(j) With the vacuum still applied, unclamp the filtration assembly and remove the filtration reservoir. Using clean tweezers, remove the analytical filter and transfer it to a petri-dish. Allow the filter to air dry before placing the cover on the petri-dish.

(k) For the beaker blank, prepare only one analytical filter by filtration of the entire 40 mL suspension.

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Table 2. Examples of the minimum number of grid openings of TEM specimens required to be examined to achieve a particular analytical sensitivity and limit of detection.

Analytical sensitivity (10^6 Fibers/g)	Limit of detection (10^6 Fibers/g)	Volume of Suspension Filtered (mL)				
		0.01	0.03	0.1	0.3	1
0.1	0.3	551	184	56	19	6
0.2	0.6	276	92	28	10	4
0.3	0.9	184	62	19	7	4
0.4	1.2	138	46	14	5	4
0.5	1.5	111	37	12	4	4
0.7	2.1	79	27	8	4	4
1	3	56	19	6	4	4
2	6	28	10	4	4	4
3	9	19	7	4	4	4
4	12	14	5	4	4	4
5	15	12	4	4	4	4
7	21	8	4	4	4	4
10	30	6	4	4	4	4

NOTES

In Table 2, it is assumed that the initial sample weight was 50 grams, the volume of water used to disperse the sample is 1 liter, the active area of the analytical filter is 199 mm², and the TEM grid openings are square with a linear dimension of 85 μm. The limit of detection is defined as the upper 95% confidence limit of the Poisson distribution for a count of zero structures. In the absence of background, this is equal to 2.99 times the analytical sensitivity. Non-zero backgrounds observed during analysis of blank filters will degrade the limit of detection.

NOTES

It is recommended to prepare several analytical filters from the suspension. If the particulate or fiber concentration is thought to be such that it is required to filter an aliquot of lower volume than 1 mL, use a dilution procedure in which 1 mL of the original suspension is transferred to a clean beaker and diluted with freshly-distilled water to a total volume of 100 mL. After stirring to ensure complete mixing, aliquots of 1 mL, 3 mL, 10 mL and 30 mL from this diluted suspension can then be filtered, corresponding to volumes of 0.01 mL, 0.03 mL, 0.1 mL and 0.3 mL of the original suspension. From the original dispersion, volumes of 1 mL and 3 mL can also be filtered, giving 6 analytical filters with a concentration range of a factor of 300. The requirement for washing of the filtration apparatus is minimized if the aliquots are filtered in order of increasing concentration.

It is beyond the scope of this method to provide detailed instructions for preparation of TEM specimens from membrane filters; these instructions are published in ISO 13794. It is recommended that aliquots of the aqueous suspension of vermiculite be filtered using the method specified in ISO 13794. Blank filters shall be checked from each lot of filters used, or the individual filters if polycarbonate filters are used they may be cleaned to remove the chrysotile,

amosite or crocidolite asbestos contamination reported to be present on this type of filter (Chatfield, 2000, and Webber, 2003). Prepare TEM specimens from the filters using the methods specified in ISO 13794. Prepare SEM specimens from the filters using the methods specified in USEPA SOP No. SRC-LIBBY-02 (Rev.1).

Blank filters shall be checked from each lot of filters used, or if polycarbonate filters are used, individual filters may be cleaned to remove asbestos contamination (Chatfield....Webber..)" Discussion and micrographs of polycarbonate filter contamination can also be found in Millette, J.R., Few, P., and Krewer, J.A., " Asbestos in Water Methods: EPA's 100.1 & 100.2 and AWWA's Standard Method 2570," Advances in Environmental Measurement Methods for Asbestos, ASTM STP 1342, M.E. Beard and H.L. Rook, Eds., American Society for Testing and Materials, 2000.

9.3.4 Examination of TEM Specimens

The number of fibrous amphiboles are counted from 10 grid openings of the TEM grid. Criteria for examination of TEM specimens are specified in ISO 10312 and ISO 13794. For the purpose of VAI analysis, only fibrous amphibole structures longer than 0.5 µm need be considered. The above ISO Standards specify that a magnification of approximately 10,000 is sufficient for determination of the concentration of asbestos structures longer than 5 µm. Classify amphiboles according to the International Mineralogical Association classification (Leake, 1997). A classification may also be obtained using procedures described by Meeker (Meeker, 2003)

9.3.5 Examination of SEM Specimens

Criteria for examination of SEM specimens are specified in USEPA SOP No. SRC-LIBBY-02 (Rev.1).

10 · DATA REPORTING

All samples must report the sample identity, the date of analysis, and the analyst.

10.1 Rapid Screening Analysis of "Sinks" to Determine Minimum Weight Percent of Fibrous Amphibole

In the test report, all relevant measurements shall be reported, including:

(a)   Initial weigh of the sub-sample;
(b)   Weight loss on drying (if applicable);
(c)   Weight of "sinks" after water separation;
(d)   Weight of hand-picked fibrous amphibole;
(e)   Assumed sensitivity of the chemical balance;
(f)   Identity of the fibrous amphibole in (d) and the method of determination including range of α and γ refractive indices for PLM analyses

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APPENDIX A: Examples of EDS spectra from Libby amphibole (Spectra by W.B. Hill, MVA, Inc.)

Reference Spectra For Libby Amphiboles
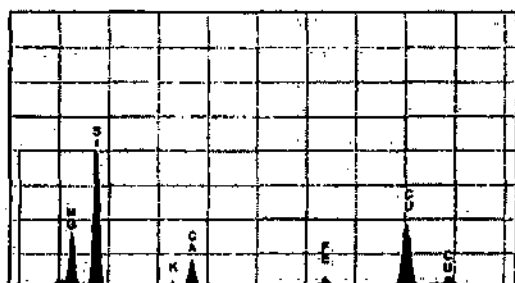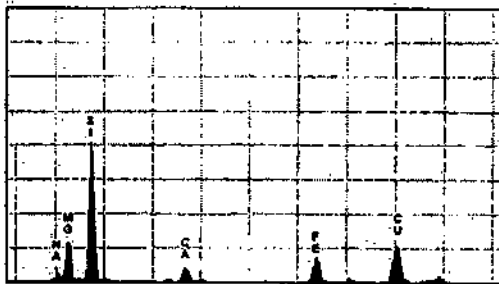
Libby Amphibole - Low Sodium   TEM: 100kv   MVA, Inc.
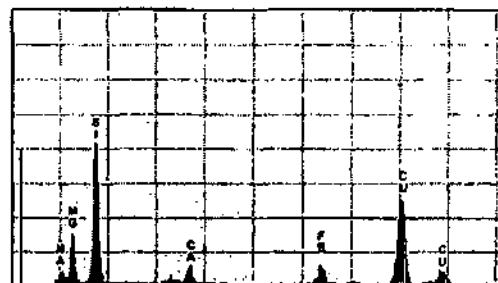
Libby Amphibole - High Sodium   TEM: 100kv   MVA, Inc.
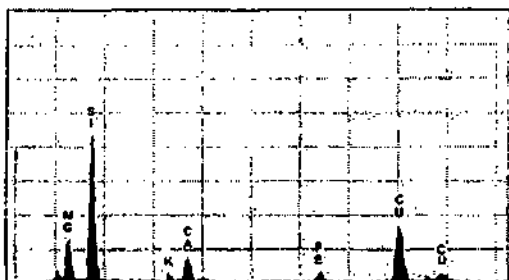
Libby Amphibole - Low Magnesium   TEM: 100kv   MVA, Inc.
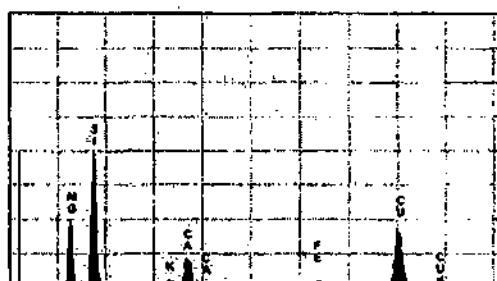
Libby Amphibole - High Magnesium   TEM: 100kv   MVA, Inc.
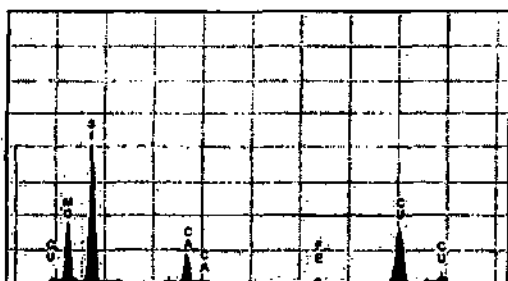
Libby Amphibole - Low Potassium   TEM: 100kv   MVA, Inc.
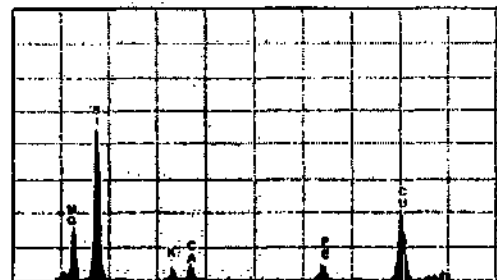
Libby Amphibole - High Potassium   TEM: 100kv   MVA, Inc.

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Reference Spectra For Libby Amphiboles
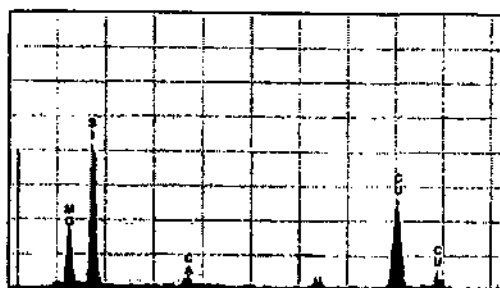
Libby Amphibole - Low Calcium   TEM: 100kv   MVA, Inc.
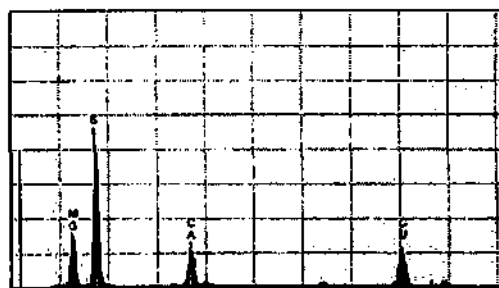
Libby Amphibole - High Calcium   TEM: 100kv   MVA, Inc.
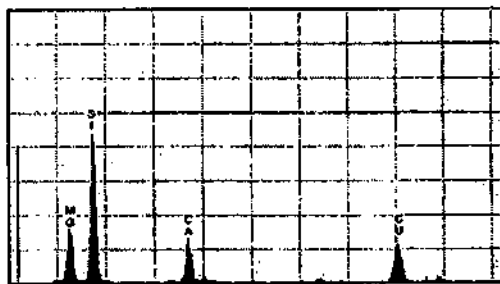
Libby Amphibole - Low Iron   TEM: 100kv   MVA, Inc.

Libby Amphibole - High Iron   TEM: 100kv   MVA, Inc.

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Reconnaissance Study of the Geology of U.S. Vermiculite Deposits— Are Asbestos Minerals Common Constituents?

U.S. Geological Survey Bulletin 2192

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Abstract

Unusually high incidences of asbestos-related mortality and respiratory disease in the small town of Libby, Montana, have been linked to amphibole mineral fibers intergrown with the vermiculite deposits mined and milled near the town from 1923 to 1990. A study conducted by the U.S. Agency for Toxic Substances and Disease Registry concluded that mortality due to asbestosis in Libby mine and mill workers and residents during 1979 to 1998 was much higher than expected for a similar Montana or United States population group. Recent medical testing of past and present mineworkers and residents of Libby showed lung abnormalities in nearly one-fifth of the adult study participants. The U.S. Environmental Protection Agency, under Superfund authority, is completing sampling and cleanup of asbestos-bearing materials in the mine, mill, and town sites. The U.S. Geological Survey is conducting a study, reviewed herein, to investigate the mineral content of other U.S. vermiculite deposits and to determine if the amphibole asbestos minerals like those found in the Libby deposits are common in other vermiculite deposits.

Introduction

Vermiculite is a general term applied to a group of platy minerals that form from the weathering of micas by ground water. Their distinctive characteristic is a prominent accordion-like unfolding and expansion when heated to between 800° and 1,100°C, depending on the composition and content of the vermiculite-bearing material. After processing (heat expansion), the vermiculite material is very lightweight and possesses fire- and sound-insulating properties. It is thus well suited for many commercial applications. The Libby (also called "Rainy Creek" or "Zonolite") mine was the world's largest producer of vermiculite during its operation.

Several varieties of the amphibole mineral group occur within the vermiculite ore deposit that was mined near Libby. U.S. Occupational Safety and Health Administration (OSHA) asbestos standards include the regulation of five amphibole varieties, when these particular mineral compositions occur as particles that fit the regulatory definition of "asbestos fiber" (slender mineral particles with a specific length:diameter ratio). Two of the regulated "amphibole asbestos" minerals— tremolite and actinolite—are common as mineral fibers in the Libby mine rocks, along with fibrous particles composed of three other members of the amphibole group (winchite, richterite, and ferro-edenite).

The U.S. Geological Survey (USGS) has recently studied the composition of 101 vermiculite-rich, archived samples collected from 62 vermiculite mines and deposits in 10 U.S. States. The samples were collected as part of a survey of the Nation's vermiculite resources in 1947, 1966-1967, and 1975-1976. At each mine or deposit that was visited, a limited number of hand samples were collected to represent the crude vermiculite material ("ore"). Thus, these samples likely do not fully represent all the materials present at a given site. In the current study, portions of each sample were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and electron probe microanalysis. Despite the reconnaissance nature of the original sampling, the mineralogical characterization of the vermiculite samples has so far yielded consistent results. These preliminary results indicate that amphibole fibers (consistent with "amphibole asbestos" as defined by OSHA) are not common in some types of vermiculite deposits, but the amphibole asbestos mineralogy similar to that found in the Libby deposit is not unique. Initial results suggest that vermiculite deposits that formed within geologic settings similar to the Libby deposit—relatively quartz deficient, potassium-, sodium- and calcium-rich igneous intrusions, typically zoned—may contain amphibole fibers with chemical compositions similar to that of the Libby deposit minerals. Also, vermiculite deposits found where masses of ultramafic rocks are cut by granite and (or) pegmatite can contain amphibole fibers. These relationships may help guide priorities for sampling, monitoring, permitting, and reclamation of active and historic vermiculite mines.

The Vermiculite-Asbestos Issue

The association of amphibole asbestos with mined vermiculite has received significant nationwide attention since November 1999, when the Seattle Post-Intelligencer newspaper reported that unusually high incidences of asbestos-related
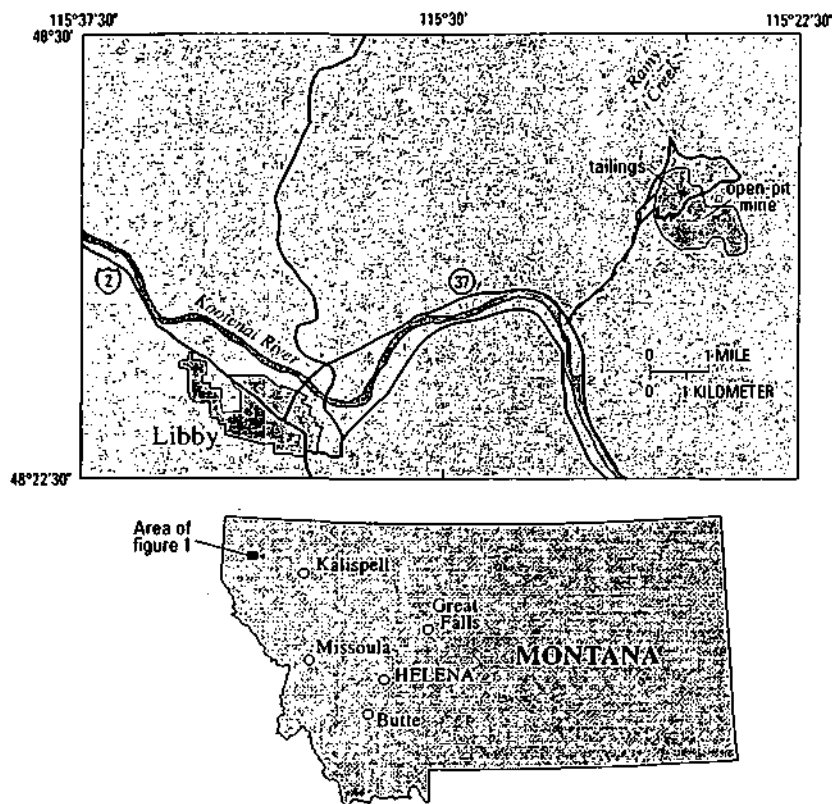
Figure 1.   Location of the Libby (Rainy Creek, Zonolite) mine near Libby, Mont., site of open-pit mining of vermiculite from 1923 to 1990.

mortality and respiratory disease occur in the small, vermiculite-mining town of Libby, Mont. (Schneider, 1999). Asbestosis and other respiratory diseases in Libby residents are thought to be directly linked to amphibole-asbestos minerals found in the vermiculite ore deposit, which was mined about 6 miles northeast of the town (fig. 1) from 1923 until mine closure in 1990 (106th Congress, 2000). The U.S. Agency for Toxic Substances and Disease Registry (ATSDR) reviewed death certificate data for Libby mineworkers and residents for the 20-year period of 1979 to 1998 (Dearwent and others, 2000). Their report concluded that "mortality in Libby resulting from asbestosis was approximately 40 to 60 times higher than expected" compared "with mortality statistics for the state of Montana and the U.S. population" (Dearwent and others, 2000). The ATSDR conducted medical tests of the mineworkers and past and present residents of Libby. Included were sets of chest X-rays, pulmonary function lung tests, and face-to-face interviews with each person to review his or her medical history. Results released in August 2001 reportedly showed lung abnormalities (such as pleural thickening or scarring of the lungs) in about 18 percent (994) of the 5,590 adults participating in the testing (McLaughlin, 2001; Smith, 2001). The U.S. Environmental Protection Agency (EPA), under Superfund authority, is sampling and performing remediation in the town of Libby, the mines and mill sites, and the surrounding area.

The Libby (also known as the "Rainy Creek" or "Zonolite") vermiculite mine was an open-pit operation that began as a modest producer in 1923 but grew to be a major part of

the world vermiculite market. The Libby mine is estimated to have supplied more than 50 percent of the world's vermiculite output based on available U.S. and world production data between 1924 and 1990 (DiFrancesco and Potter, 2001). It processed an estimated 20,000 tons (18,000 metric tons (t)) in 1940, 150,000 tons (136,000 t) in 1950, and 200,000 tons (180,000 t) in 1970 (McDonald and others, 1986).

Regulatory Definitions of Amphibole Asbestos

The term "asbestos" is a commercial term that refers to a group of silicate minerals that will easily separate into strands of thin, strong fibers that are flexible, heat resistant, and chemically inert, and thus well suited for applications such as heat insulation (Cossette, 1984; Ross, 1981; Ross and others, 1984; Skinner and others, 1988; Zoltai, 1981). In a mineralogical sense, the two groups of asbestos minerals are (1) serpentines, with the only asbestiform variety called chrysotile, and (2) specific amphiboles, including crocidolite (riebeckite asbestos), cummingtonite-grunerite asbestos (commercially called amosite), and the asbestiform varieties of tremolite, anthophyllite, and actinolite. According to OSHA asbestos regulation standards, in order to determine the "asbestos" content of a particular mineral assemblage, an analyst should count mineral particles that

1. Are 5 μm (micrometers) or longer in length and display asbestos growth habit (length:diameter aspect ratios of at least 3:1, usually exceeding 100:1);

2. Lack longitudinal striations that suggest the particle is a "cleavage fragment" (Campbell and others, 1979; Zoltai, 1981), which are exempt from regulation based on a 1992 OSHA ruling (Occupational Safety and Health Administration, 1992, p. 24320); and

3. Are composed of one of the six regulated asbestos "mineral" phases—chrysotile, crocidolite (riebeckite), cumming-tonite-grunerite ("amosite"), tremolite, anthophyllite, and actino-lite. These mineral compositions and morphologies were encountered in occupational exposures associated with asbestosis.

The OSHA asbestos regulation also notes: "Asbestos fibers exist in bundles that are easily parted, show longitudinal fine structure and may be tufted at the ends showing 'bundle of sticks' morphology" (Title 29, Code of Federal Regulations, 1999 (29 CFR 1910.1001)). Another guideline, although apparently unofficial in its application, is that asbestos fibers are flexible, typically indicated by long, thin fibers that appear to bend but not break. True asbestos is thought to be extremely flexible and not brittle (Zoltai, 1981).

For this study, we applied the terms "fiber" or "fibrous" in accordance with OSHA asbestos regulation standards, which define asbestos fiber as: "A particle that is 5 μm or longer, with a length-to-width ratio of 3 to 1 or longer" (Title 29, Code of Federal Regulations, 1999 (29 CFR 1910.1001)). We further considered "fibers" to include only those mineral particles with diameters visually estimated to be 3 μm or less, because regulatory agencies worldwide have generally agreed that at about 3 μm or less the mineral fibers are most hazardous to the human respiratory system. (See Cossette, 1984, p. 34–36.)

Study Goals

Careful analyses and characterization of the Libby asbestos minerals will (1) complement toxicological studies that examine the effects of these minerals on the human respiratory system, and (2) assist regulatory agencies in the identification of potentially dangerous asbestiform amphiboles relative to less hazardous amphiboles. For example, the U.S. OSHA and the U.S. EPA asbestos regulations (Title 40, Code of Federal Regulations, Part 61 and Part 763; Title 29, Code of Federal Regulations, Part 1910 and Part 1926) do not specify asbestiform richterite and asbestiform winchite, which are common constituents of the Libby deposits, as regulated asbestos minerals. (See Wylie and Verkouteren, 2000; Verkouteren and Wylie, 2000.)

A study is underway by the USGS to analyze the mineralogy of vermiculite-rich samples collected from 62 U.S. vermiculite mines and deposits. The study is initially being conducted by reconnaissance sampling and analyses using XRD, SEM, EDS, and electron probe microanalysis. The purpose of the study is to determine how common the amphibole asbestos minerals, like those found at Libby, are in other vermiculite deposits, and if they occur in similar morphologies and compositions.

The Geology and Uses of Vermiculite

Vermiculite Geology

Vermiculite is a general term applied to a group of platy, mica-like, hydrated silicate minerals with the general formula $(Mg,Fe,Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4H_2O$. Most vermiculite group minerals are the products of aqueous alteration of micas, primarily the biotite subgroup (annite-phlogopite); they pseudo-morph the platy morphology of the replaced mica. Typically, the biotite grains alter to hydrobiotite or chlorite, then to vermiculite (Bush, 1976). Vermiculites encompass a wide range of chemical compositions, vary in color from light yellow to green to brown to black, and generally have a bronze hue. Their distinctive characteristic is a prominent exfoliation when heated from 800° to 1,100°C. When heated, the vermiculite plates expand at right angles to the cleavage (accordion-like) as the contained water is converted to steam. This forms elongated, worm-like, light-weight particles that trap air. Individual particles can expand from 6 to as much as 30 times their original volume in the longest dimension (fig. 2).

Vermiculite forms from the low-temperature, weathering alteration of micaceous minerals in the zone of ground-water circulation (Bush, 1976). Thus, commercial vermiculite deposits require an igneous or metamorphic host rock that contains an abundance of large mica crystals, especially biotite or phlogopite, which have interacted with ground water and (or) surface waters. Biotite forms in a wide range of igneous and metamorphic environments, and phlogopite occurs in metamorphosed carbonate and ultramafic rocks. Bassett (1959) attributed the formation of biotite and asbestiform amphiboles in the Libby deposits to the alteration of augite (in pyroxenites) by high-temperature silica-rich solutions. Vermiculite formation clearly postdates the high-temperature rock-forming processes (Bassett, 1959; Bush, 1976).

Bush (1976) categorized vermiculite deposits into three broad groups, as follows: (1) deposits within large ultramafic intrusions, such as pyroxenite plutons, many of which are zoned and are cut by syenite or alkalic granite and by carbonatitic rock and pegmatite; (2) deposits associated with small to large ultramafic intrusions, such as dunite and unzoned pyroxenite and peridotite, cut by pegmatite and syenitic or granitic rocks; and (3) deposits in ultramafic metamorphic rocks. The Libby deposits are of the first deposit type.

Vermiculite Uses and Production

Processed (heat-expanded) vermiculite material is very light weight and has fire- and sound-insulating properties. Therefore, it is useful material for many commercial applications. Processed vermiculite is commonly used as a light-weight aggregate in concrete or plaster to make low-weight, sound-deadening, fire-resistant walls, boards, panels, and coatings. Other common applications are in horticulture and agriculture, as an additive to mulch, potting soils, and growing mixes, and as a carrier and extender for fertilizers, pesticides, and herbicides (Potter, 2001).

Figure 2. Examples of raw vermiculite (left) and processed (heat-expanded) material (right). When heated to 800°–1,100°C, the water naturally contained between the layers of the vermiculite structure is converted to steam. The steam pushes the crystal layers apart, expanding the vermiculite material from 6 to as much as 30 times its original thickness.
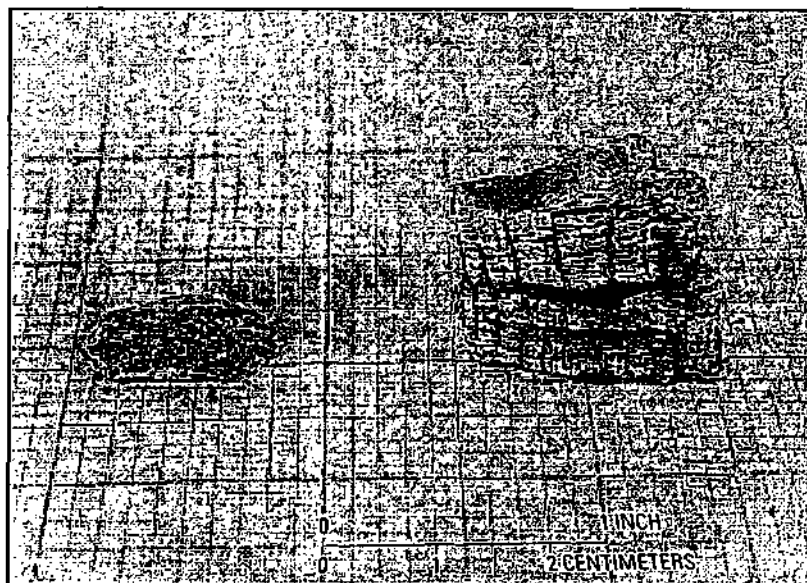
In 1999, South Africa led the world in production of vermiculite (218,000 t), followed by the United States (175,000 t), with much smaller production (each with 40,000 t or less) from People's Republic of China, Russia, Brazil, and several other countries (Potter, 2001). Three operations currently (2002) produce vermiculite in the United States—one operated by W.R. Grace & Co. near Enoree, S.C., one operated by Virginia Vermiculite Ltd. in Louisa County, Va., and one operated as a Virginia Vermiculite subsidiary near Woodruff, S.C.

Amphibole Mineralogy of the Libby Vermiculite Deposit

The Libby deposit contains amphiboles of several compositions that form intergrowths with the vermiculite and gangue rocks (fig. 3). Using current amphibole nomenclature, the amphibole compositions include winchite, richterite, tremolite, actinolite, ferro-edenite, and magnesio-arfvedsonite (this study; Wylie and Verkouteren, 2000). Winchite, richterite, tremolite, and actinolite represent subtle crystallographic and chemical compositional variations closely related to the tremolite-actinolite amphibole series (table 1), as explained by Wylie and Verkouteren (2000) and Verkouteren and Wylie (2000). Winchite, richterite, tremolite, actinolite, and ferro-edenite occur as blocky and elongate crystals, stubby and acicular cleavage fragments, and as fibrous (asbestiform) particles in the ores and gangue of the Libby vermiculite deposit (table 1; fig. 3). Magnesio-arfvedsonite, tentatively identified in samples from Libby, is found only as blocky crystals, and thus is not listed in table 1 as one of the fibrous amphibole minerals found in U.S vermiculite deposits. Fibrous winchite and richterite at other localities, as at Libby, are found associated with altered alkaline igneous rocks (Wylie and Verkouteren, 2000).

USGS Reconnaissance Study

The USGS is assembling a growing set of currently more than 100 samples of vermiculite. Most were collected from site visits to deposits throughout the U.S. by A.L. Bush in 1947, 1966-1967, and 1975-1976, and mostly during active mining. Additional samples were collected in 2001 at abandoned mine sites. The study samples are grab samples of vermiculite-bearing material ("ore") and are not fully representative of the materials mined or processed, or found in outcrop, at each particular deposit. Also, gangue and bedrock materials generally are not represented. Splits from 101 samples have been analyzed using SEM, EDS, and XRD methods. The samples analyzed are from deposits in Georgia (1 sample), South Carolina (27), North Carolina (14), Texas (21), Arizona (2), California (3), Wyoming (15), Idaho (4), Colorado (10), and Montana (4 non-Libby samples). The analytical results are compared to those for a representative suite of 30 samples that were collected from former mining operations at Libby.

Of the 101 vermiculite samples analyzed by SEM, 13 samples representing five vermiculite-rich districts were found to contain numerous fibrous amphibole particles. Two Colorado vermiculite districts—the Gem Park Complex, which straddles part of the Custer and Fremont County boundary, and the Powderhorn district in Gunnison County—contain an abundance of fibers semiquantitatively determined to be winchite, richterite, and riebeckite (fig. 4). A deposit in the Gold Hill district in Latah County, Idaho, contains abundant fibers of actinolite on the surface of vermiculite grains. Samples from the Smith mine vermiculite deposit in Converse County, Wyo., were found to contain fibrous tremolite and anthophyllite particles within a serpentine groundmass (fig. 5). The Addie district in Jackson County, N.C., contains abundant fibrous anthophyllite and tremolite associated with the vermiculite and talc. Amphibole fibers were found in minute amounts (a few fibers each) in 11 other samples from
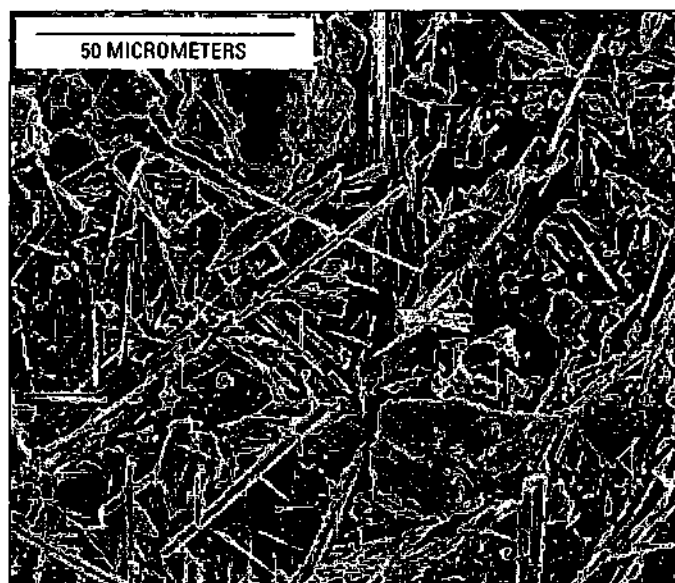
Figure 3. Scanning electron microscope (SEM) photograph of vermiculite ore material collected from an open pit of the Libby mine, Montana. The platy minerals have been identified as vermiculite, hydrobiotite, biotite, and phlogopite. Fibrous particles are amphibole phases with compositions identified as winchite, richterite, tremolite, actinolite, and ferro-edenite (table 1).

Table 1.   Ideal compositions for the fibrous amphibole minerals found in U.S. vermiculite deposits.

[Cation ratios from Leake and others, 1997]

Mineral	Ideal cation ratios
winchite	$(Ca, Na)Mg_4(Al, Fe^{3+})Si_8O_{22}(OH)_2$
richterite	$Na(Ca, Na)Mg_5Si_8O_{22}(OH)_2$
tremolite	$Ca_2(Mg, Fe)_5 Si_8O_{22}(OH)_2$ $Mg/(Mg+Fe^{2+}) = 1.0 - 0.9$
actinolite	$Ca_2(Mg, Fe)_5 Si_8O_{22}(OH)_2$ $Mg/(Mg+Fe^{2+}) = 0.5 - 0.89$
ferro-edenite	$NaCa_2Fe^{2+}_5 Si_7AlO_{22}(OH)_2$
riebeckite (crocidolite)	$Na_2(Mg, Fe^{2+})_3Fe^{3+}_2 Si_8O_{22}(OH)_2$ $Mg/(Mg+Fe^{2+}) < 0.5$
anthophyllite	$(Mg, Fe^{2+})_7Si_8O_{22}(OH)_2$ $Mg/(Mg+Fe^{2+}) = 1.0 - 0.5$

nine deposits scattered throughout the U.S. The remaining vermiculite samples analyzed either lacked amphiboles or contained amphiboles that appear nonfibrous; these samples correspond to 48 deposits that generally fit the geologic characteristics of Bush's (1976) "type-2" or "type-3" deposits.

Thus far in the study, four of the six vermiculite districts that show abundant amphibole fibers associated with the vermiculite—the Libby vermiculite deposit, two Colorado areas, and one Idaho deposit—all have similar geologic settings. The Libby (Rainy Creek or Zonolite) deposit formed by alteration of a large zoned pyroxenite pluton having a central biotite-rich pyroxenite core. A younger mass of syenite cuts the outer

zones of the pluton, and alkalic syenite dikes cut the biotitite core. A nearby small mass of nepheline syenite is present. Fenitization of the metasedimentary rocks surrounding the pluton suggests that a carbonatitic mass occurs at depth (Boettcher, 1967). One of the vermiculite-rich Colorado districts containing fibers is hosted by a zoned pluton—the Gem Park Complex—consisting mostly of pyroxenite and gabbro, cut by abundant carbonatite dikes and irregular masses with associated fenite (Parker and Sharp, 1970). The Gem Park Complex is cut further by minor dikes and bodies of lamprophyre, syenite porphyry, and nepheline syenite pegmatite. The complex is interpreted to contain a large carbonatite body at depth (Parker and Sharp, 1970; Armbrustmacher, 1984). The other Colorado vermiculite district with fibers is hosted by the Iron Hill stock (or "complex"), also described as a carbonatite intrusion. This stock is zoned, composed of mostly pyroxenite in the core. The stock's core is cut by nepheline-pyroxene garnet-rich rock. Sodic syenite and nepheline syenite intruded along the borders of the stock, and late dikes of nepheline gabbro and quartz gabbro cut the entire stock complex (Larsen, 1942; Temple and Grogan, 1965; Nash, 1972; Olson, 1974; Hedlund and Olson, 1975; Olson and Hedlund, 1981). The Idaho vermiculite deposit that contains actinolite fibers is hosted by a zoned hypabyssal stock—the Gold Hill stock. This stock has a core of mainly hornblende syenite with subordinate hornblende monzonite and hornblende syenodiorite (Tullis, 1944). Pyroxenite and syenite dikes are spatially associated with the stock and vermiculite deposit (Tullis, 1944).

The Smith mine vermiculite deposit in Wyoming contains tremolite and anthophyllite fibers formed at the contact zone between a granitic intrusion and massive serpentinite (Hagner, 1944). The amphibole fibers and biotite grains (which converted to vermiculite) apparently formed in a zone of metasomatic chemical exchange along the contact of the intruding granite with serpentine-rich country rocks. The North Carolina district—the Addie district—is associated with the Day
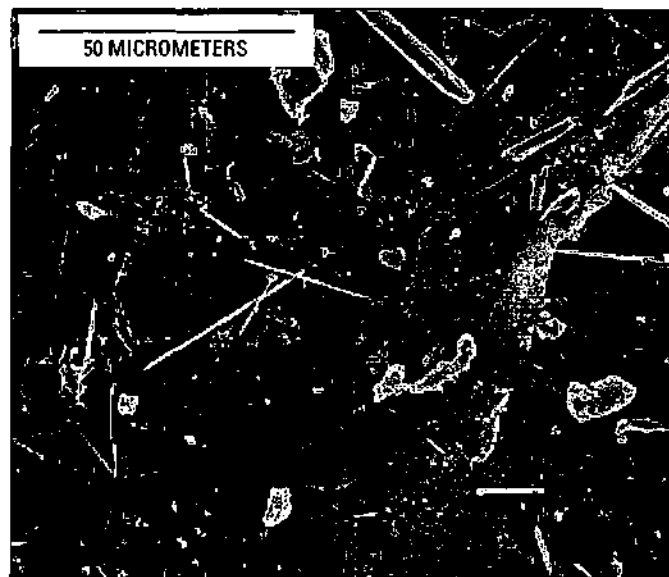
Figure 4. SEM photograph of vermiculite-rich material collected from Gem Park Complex, Colorado. Platy minerals visible are vermiculite and hydrobiotite. Fibrous particles are amphibole phases with compositions identified as winchite, richterite, and riebeckite (table 1).

Book dunite deposit and contains alteration zones composed of vermiculite (weathered phlogopite), fibrous tremolite and anthophyllite, and talc along serpentine-rich contacts between dunite masses and intruding pegmatites (Murdock and Hunter, 1946; Kulp and Brobst, 1954). The general geologic characteristics of these Wyoming and North Carolina vermiculite deposits correspond to Bush's (1976) "type-2" deposits. El Shazly and others (1975) described asbestos-vermiculite deposits in Egypt, and summarized similar deposits elsewhere, whose geologic characteristics are very similar to the Wyoming and North Carolina "type-2" vermiculite deposits.

Conclusions

The results of this mineralogical survey are preliminary, and the study sample set was collected in a reconnaissance fashion; therefore, additional, more representative sampling is planned. The results of this preliminary survey are consistent and suggest that fibrous amphiboles, in more than trace amounts, may not be common in the ore zones of some types of vermiculite deposits. However, the asbestiform amphibole mineralogy of the Libby deposit is not unique. The initial results suggest that vermiculite deposits associated with zoned, alkalic/calcic, quartz-poor plutons, especially those with characteristics of carbonatite intrusions, may be likely to contain fibrous amphiboles. Also, vermiculite deposits associated with ultramafic bodies cut by granite and (or) pegmatite deserve scrutiny, because contact metamorphic reactions along these contact zones often form serpentine-rich bodies that contain an abundance of amphibole fibers. These relationships may help guide priorities for sampling, reclamation, permitting, and monitoring of active and inactive vermiculite mines.

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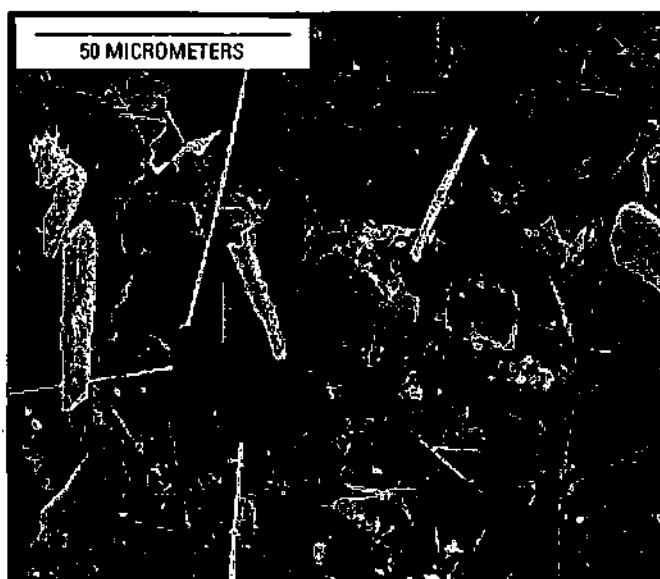
Figure 5. SEM photograph of a sample collected from Smith mine deposit, Wyoming. The fibrous particles have been identified as tremolite. Groundmass is mainly serpentine.

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VDI 3492(2004-10) Part 2
Indoor Air Pollution Measurement: Measurement of Inorganic Fibrous Particles Measurement Planning and Procedure Scanning Electron Microscopy Method

Substantial amounts of airborne, respirable fibres can be released into the indoor atmosphere from fibre-containing materials, which were used for a variety of applications in buildings, such as thermal insulation, flame retardancy or sound absorption, as a result of deterioration, vibrations, air movements or mechanical impact. The assessment of the resulting indoor air contamination by fibres requires a measurement method for determining fibre concentrations, which takes the specific indoor characteristics into account.

General aspects concerning the procedure of indoor air pollution measurements are specified in Guideline VID 4300 Part 1. Guideline VDI 3492 Part 2 translates these general aspects into the specification of a measurement methods for the determination of the numerical concentration of airborne inorganic fibrous particles. The sampling strategy takes specific indoor features into account; analysis and evaluation of results follow the procedure specified in Guideline VDI 3492 Part 1, which was established primarily for ambient air measurements and therefore had to be modified as follows:

-   the size spectrum of the fibres to be counted is limited to fibres equal to or greater than 5 μm in length.
-   The fibre type classification system is extended with respect to man-made mineral fibres.

Furthermore some fibre counting rules and certain aspects of the criteria for fibre identification have been modified.

The essential field of application of this Guideline is air monitoring in conjunction with the demolition, renovation and maintenance work concerning materials containing asbestos. Measurements in work areas while working on fibre containing materials are, however, outside the scope of this Guideline.

In principle this Guideline is applicable to the measurements which serve to establish the concentration of airborne fibres and to identify the type of fibres unless other regulations are in place.

In cases in which the current fibre concentration cannot be measured during normal usage of the rooms to be examined it is necessary to simulate the conditions of usage in order to bring about a fibre concentration in the indoor air, which can be considered representative of actual usage. This Guideline specifies appropriate methods for the simulation of the conditions of usage in order to enable the measuring results to be compared.

In view of the complex and sophisticated methods a specific section gives practical information to the user of this Guideline which serves to eliminate potential sources of error and thus substantially contributes to the reliability of the measuring results.

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Amphibole asbestos from Libby, Montana: Aspects of nomenclature

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ABSTRACT

Richterite-asbestos and winchite-asbestos are not listed in the federal regulations governing asbestos. However, asbestiform winchite is found in the gangue at the Libby, Montana, vermiculite deposit, where asbestos-related diseases have been reported among the miners and millers. Changing amphibole nomenclature, uncertainties in Fe^{2+}/Fe^{3+}, and natural compositional variability result in samples of the asbestiform amphibole from Libby being variably classified as soda tremolite, richterite, sub-calcic actinolite, and winchite. A classification of winchite-asbestos is assigned for two samples of Libby asbestos analyzed for this report, consistent with the most recent International Mineralogical Association classification system. Although some of the unit-cell parameters and optical properties reported here are distinctive, others are very similar to the tremolite-actinolite series.

INTRODUCTION

The U.S. Occupational Safety and Health Administration (OSHA) and the U.S. Environmental Protection Agency (EPA) have regulated asbestos since the early 1970s (summarized by Vu 1993). The current regulations specify chrysotile and the asbestiform habit of five amphiboles: tremolite, actinolite, anthophyllite, riebeckite (listed as crocidolite) and cummingtonite-grunerite (listed as amosite) (Title 40, Code of Federal Regulations, Part 61 and Part 763; Title 29, Code of Federal Regulations, Part 1910 and Part 1926[1]). These minerals were known at the time the regulations were first written to have been mined commercially as asbestos. Although there have been modifications to the regulations since they were first promulgated, most notably to clarify that cleavage fragments are not asbestos (Federal Register 1992), the minerals that are regulated have not changed. In particular, the sodic-calcic amphiboles winchite and richterite are not regulated.

An asbestiform amphibole occurs as a gangue mineral in the Zonolite® vermiculite ore body in Libby, Montana, which was mined from 1923 to 1990. Estimates of the abundance of the amphibole in the unprocessed ore range from 0 to ≈ 5 wt% (Atkinson et al. 1982). An elevated incidence of mesothelioma, the hallmark of asbestos exposure, has been reported among the miners and millers of Zonolite® in several studies that were summarized by Ross et al. (1993). In late 1999 and early 2000, many deaths alleged to be due to asbestos exposure in Libby were reported in the popular press, stimulating Congressional oversight (106th Congress 2000). Of particular significance for the regulatory community is the identity of the asbestiform amphibole.

The asbestiform amphibole at Libby has been referred to under a variety of names, including tremolite, actinolite, soda tremolite, richterite, and winchite. The current nomenclature used in the popular press and by the residents of Libby is tremolite, or tremolite/actinolite. Deer et al. (1963) give an analysis of an amphibole from Libby (taken from Larson 1942) that they identify as "richterite (soda tremolite)."

In the amphibole classification system of Deer et al. (1963), Miyashiro's (1957) classification of the alkali amphiboles was generally adopted. However, of particular significance to the Libby amphibole, Deer et al. (1963) used the name richterite in place of soda tremolite, dividing tremolite from richterite at $NaCa_{1.5}$, (they considered winchite to be a subset of richterite). The International Mineralogical Association (IMA) classification (Leake 1978) continued the use of richterite in place of soda tremolite and added specific chemical parameters for distinguishing the actinolite series from richterite and for applying the name winchite. The parameters for richterite were $^{B}(Ca + Na) \geq 1.34$ atoms per formula unit (apfu) and $0.67 < ^{B}Na < 1.34$ apfu (classifying the amphibole as a member of the sodic-calcic group) and $Si > 7.5$ apfu and $^{A}(Na+K) \geq 0.5$ apfu. By the IMA 1978 classification scheme, winchite is also a member of the sodic-calcic group and is distinguished from richterite by $^{A}(Na + K) < 0.5$ apfu. Members of the actinolite series belong to the calcic group and have $^{B}(Ca + Na) \geq 1.34$ apfu and $^{B}Na < 0.67$ apfu. Another relevant evolution in the nomenclature was the division between tremolite and actinolite; according to Deer et al. (1963), tremolite contained between 0 and 20% ferro–actinolite while according to the IMA, tremolite contained no more than 10% ferro–actinolite. The most recent nomenclature changes in Deer et al. (1997) and the revised IMA classification (Leake et al. 1997) changed the positions of the subdivisions to fit a 50% rule. Under these changes, $^{B}(Na +$

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[1]Regulations dealing with asbestos can be obtained through the websites maintained by OSHA (www.osha.gov) and the EPA (www.epa.gov).

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Ca) ≥ 1.0 apfu is now used to define the calcic and sodic-calcic groups, and the calcic group has $^BNa < 0.50$ apfu.

RESULTS

Two samples of asbestiform amphibole from Libby were analyzed following the experimental procedures detailed in Verkouteren and Wylie (2000). Chemical compositions, cell parameters, and optical properties are given in Table 1. One of the samples had been in our collection for several years; the other was obtained recently. Sample 1 is relatively pure, loose fiber and sample 2 was collected from the mine dump and is composed primarily of asbestiform amphibole. In both cases, the fibers are light green and asbestiform. The wt% Fe (analyzed as FeO) was converted to formula proportions of cations assuming first all Fe^{2+} and then all Fe^{3+}. It seems likely that at least some portion of the iron is trivalent, as more than 8.0 apfu Si cannot be accommodated in the tetrahedral sites. Hence, the "true" formulae must lie somewhere between these two extremes.

Because $^B(Na + Ca) \geq 1.0$ apfu this amphibole is either a sodic-calcic or a calcic amphibole. If all the iron is Fe^{2+}, then $^BNa = 0.63$ or 0.61 apfu, and according to Miyashiro (1957) the amphibole should be called soda tremolite. According to Deer et al. (1963), it would probably be richterite. According to Leake (1978), it would be sub-calcic actinolite, and according to Deer et al. (1997) and Leake et al. (1997), it would be winchite. If all the iron is Fe^{3+}, ^BNa increases to 0.75 or 0.67 apfu and according to Leake (1978), Deer et al. (1997) and Leake et al. (1997), it would be winchite. The chemical composition of the Libby amphibole as reported by Larson (1942) corresponds to a current classification of richterite.

Deer et al. (1963) chose $NaCa_{1.5}$ as the dividing line between richterite and tremolite because it was consistent with a "relatively sudden" change in optical properties, specifically a decrease in birefringence, stronger pleochroism, lower indices of refraction, and smaller optic axial angle. The refractive indices given in Table 1 are different for the two samples, consistent with the change in $1 - Mg/(Mg + Fe + Mn)$. Comparison of the optical properties to those of the actinolite series (Verkouteren and Wylie 2000) indicates that, for both samples, n_α is high and n_γ is low, although not statistically outside the population of actinolite samples. The birefringence given in Table 1 is much lower than any actinolite sample in Verkouteren and Wylie (2000) and is a clear outlier; this is also true for the birefringence of the Libby amphibole given by Larson (1942). No difference exists between the optic axial angle given in Table 1 and the actinolite series; however, the optic axial angle for the Libby amphibole reported by Larson (1942) is distinctly smaller than that of corresponding actinolites.

Comparison of the lattice parameters to those of the actinolite series (Verkouteren and Wylie 2000) indicates that, for both samples, a and c are at or within the 95% prediction limits for actinolite, but b is outside the lower 95% prediction limit by more than 0.025 Å. The values of a are high given a Ca value of 1.3 apfu; these samples would fall into an anomalous region in the actinolite series where a and Ca are positively correlated (Verkouteren and Wylie 2000), and we would predict an a of 9.83 Å or lower. The values of β for the Libby samples are consistent with the actinolite series and the positive correlation of β and Ca. The potassian winchite-asbestos described by Wylie and Huggins (1980) has a larger a dimension, a smaller b dimension, and the same c dimension when compared with the actinolite series. Similarly, the three non-Ti bearing richterites in Oberti et al. (1992) have larger a dimensions, smaller b dimensions, and the same c dimensions when compared to the actinolite series.

TABLE 1. Chemical composition, optical properties, and cell parameters of 2 samples of winchite-asbestos, Libby, Montana. (1σ errors in parentheses)

Oxide	wt%			apfu§, all Fe^{2+}		apfu§, all Fe^{3+}	
	Sample 1*	Sample 2†		Sample 1	Sample 2	Sample 1	Sample 2
SiO_2	56.6(4)	56.1(2)	Si	8.04	8.01	7.92	7.92
TiO_2	n.d.	n.d.	^{IV}Al	–	–	0.08	0.07
Cr_2O_3	n.d.	n.d.	ΣT	8.04	8.01	8.00	8.00
Al_2O_3	0.5(1)	0.4(2)	^{VI}Al	0.09	0.07	0.01	–
FeO	6.0(6)	4.2(4)	Mg	4.28	4.45	4.21	4.41
MnO	0.1(0)	0.3(3)	Fe	0.72	0.50	0.71	0.50
MgO	20.2(5)	21.0(4)	Mn	0.01	0.03	0.01	0.03
CaO	8.3(10)	8.8(2)	ΣC	5.10	5.05	4.94	4.94
Na_2O	3.2(8)	3.4(2)	ex. C	0.10	0.05	–	–
K_2O	0.7(1)	0.8(2)	Ca	1.27	1.34	1.25	1.33
Total	95.6	95.0	^BNa	0.63	0.61	0.75	0.67
			ΣB	2.00	2.00	2.00	2.00
			^ANa	0.25	0.33	0.12	0.26
			^AK	0.13	0.15	0.13	0.15
			ΣA	0.38	0.48	0.25	0.41
		1-Mg/(Mg+Fe+Mn)		0.15	0.11		

Notes: optical properties: Sample 1: $n_\alpha = 1.621(1)$, $n_\beta = 1.631(1)$, $n_\gamma = 1.637(1)$, $c \wedge Z = 15.8(0.5)°$. Sample 2: $n_\alpha = 1.618(1)$, $n_\beta = 1.628(1)$, $n_\gamma = 1.634(1)$, $c \wedge Z = 15.8(0.5)°$ $\delta\ddagger = 0.016$, $2V_z\ddagger = 104.9$.
Cell dimensions: Sample 1: $a = 9.855(1)$ Å, $b = 18.032(1)$ Å, $c = 5.288(3)$ Å, $\beta = 104.54(2)°$. Sample 2: $a = 9.861(2)$ Å, $b = 18.003(5)$ Å, $c = 5.276(6)$ Å, $\beta = 104.37(4)°$.
* Average of 6 analyses.
† Average of 3 analyses.
§ Calculated on the basis of 23 O atoms.
‡ Calculated from the measured refractive indices.

DISCUSSION

The composition of the Libby asbestiform amphibole as given in Table 1 is consistent with an identification of winchite-asbestos, based on Leake et al. (1997). The samples can be identified as winchites despite the uncertainty in site occupancies resulting from the unknown oxidation state of Fe. The b lattice dimension and the birefringence are consistent with what is known about winchite (and richterite) and are distinct from actinolite. Ross et al. (1993) report that both tremolite and richterite asbestos fibers were found in a specimen of Libby vermiculite. Our two samples were collected approximately ten years apart, and probably from different areas in the mine, and both are winchites, although our sample 2 is close to richterite in composition ($\Sigma A = 0.48$ to 0.41 apfu). Given the fact that the Libby amphibole reported by Larson (1942) is a richterite, it is possible that the amphibole composition ranges from winchite to richterite, and possibly to actinolite, throughout the vermiculite deposit. Asbestiform winchite and richterite are also known from other localities, where they are similarly associated with the alteration of alkali igneous rocks (Wylie and Huggins 1980; Deer et al. 1997).

It is unfortunate that a regulatory decision could hinge on such details as the amount of ^{B}Na and the choice of classification scheme. While the distinctions among amphiboles are important from a scientific standpoint, they do not add significantly to the regulatory terminology unless they are correlated with risk assessment. There are data that show differences in disease potential among different minerals with similar morphology, such as between talc and tremolite (Guthrie and Mossman 1993), but it is clear that the asbestiform winchite in Libby, Montana poses a health threat (106th Congress 2000). From an analytical standpoint, the identification of the specific asbestiform mineral is necessary for complete characterization of the asbestos component in any sample. The regulatory requirement to identify the mineral can be addressed by providing reference values for known asbestiform amphiboles, which was, in part, the impetus behind the study described in Verkouteren and Wylie (2000) and the current note. It would be reasonable for the regulations to be revised to provide a broader description of asbestiform amphiboles to avoid similar hair-splitting problems in the future.

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